THE JOURNAL
OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. XLVII AUGUST 1952 No. 8

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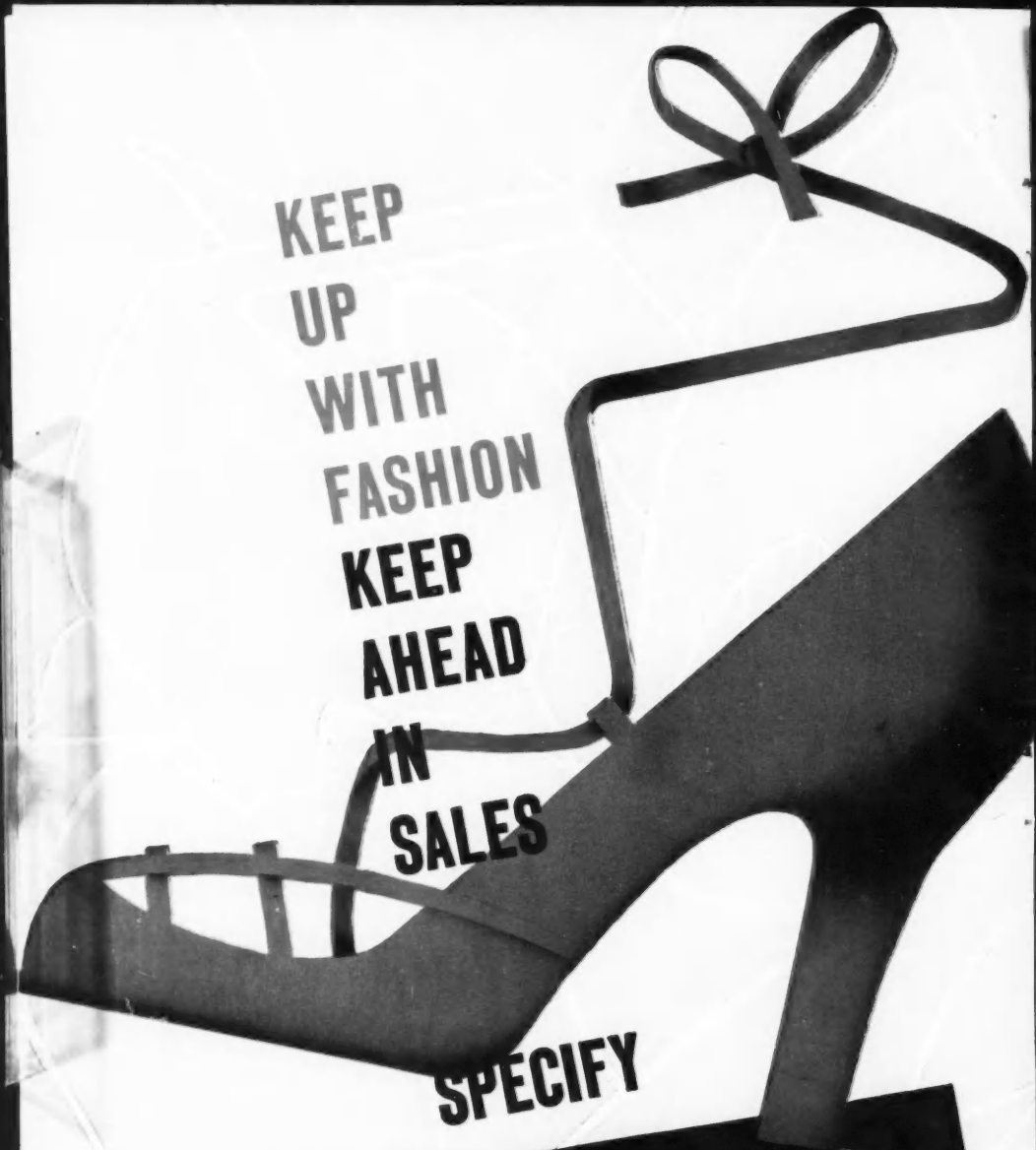

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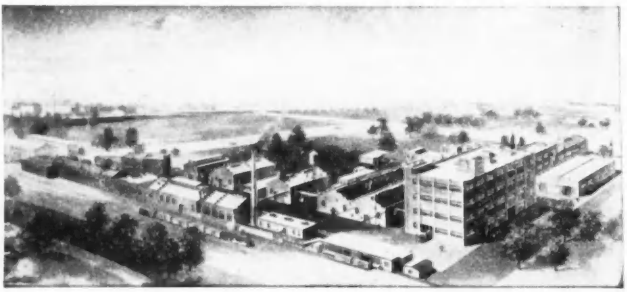

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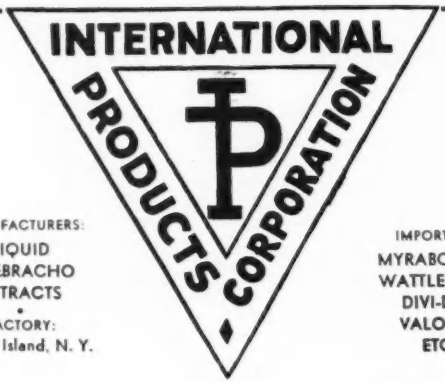

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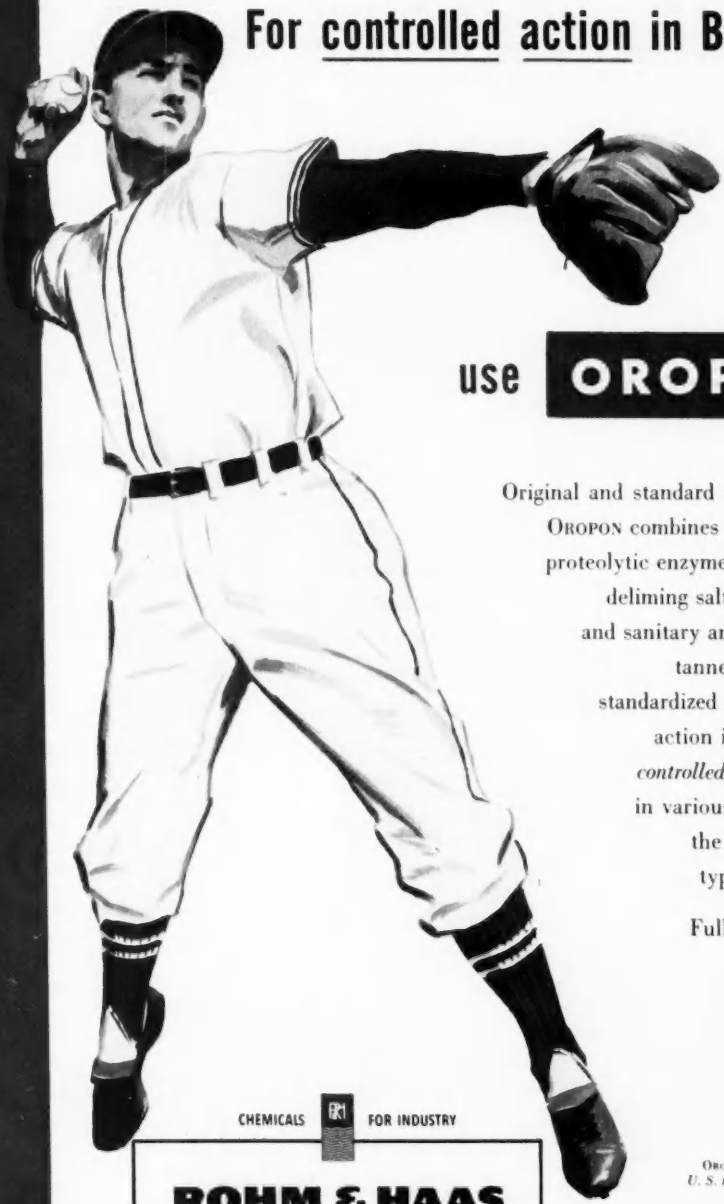

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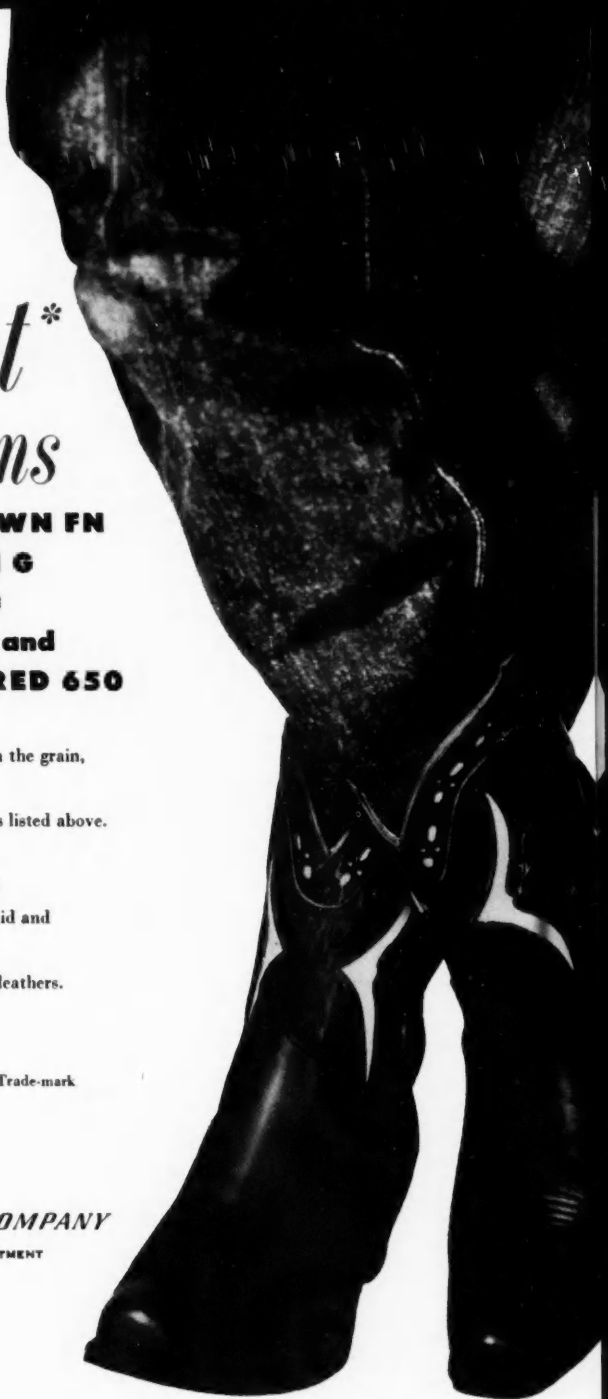

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VOL. XLVII AUGUST 1952 No. 8

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SECRETARY'S NOTICE

At a business session on June 2, 1952, the membership voted to accept as provisional the method for Hide Substance Determination, as published in the January 1952 issue of the Journal.

This method now becomes a provisional method.

Fred O'Flaherty, *Secretary*

ACKNOWLEDGMENT OF ELECTION TO LIFE MEMBERSHIP

To Council:

American Leather Chemists Association

It is with great appreciation that we acknowledge the great honor bestowed upon us in becoming Life Members.

The pleasure and surprise was so overwhelming that we were unable to adequately express our appreciation at the time of presentation. We therefore take this opportunity to thank Council and our fellow members for this honor.

We shall continue our efforts in behalf of the Association to the fullest extent of our ability.

Yours very sincerely,

Casper Drueding – Tom Faust

THE FORTY EIGHTH ANNUAL MEETING

The Forty Eighth Annual Meeting of the Association was held at The New Ocean House, Swampscott, Mass., from June first to fourth inclusive. Over four hundred members and more than one hundred wives were registered.

The choice of the New Ocean House as the Convention site was indeed an excellent one from all angles. It is sufficiently convenient to Boston and other points of historical interest so as to afford diversionary trips to these places, yet far enough distant from them that they do not inferfere with Convention interests. On all sides were heard comments favorable to the Convention Committee and the hotel management. While Mr. Thayer had functioned until March, during which time he had done the preliminary work in setting up the Convention, the final details were left to Mr. Kirk, the new chairman. Both are to be commended for the excellent job they did to make the Meeting so successful.

Technical Committee meetings were held during the afternoon and evening of June first. These committees have an important place in our Association, and are here listed with their respective chairmen. Coordinator of all Committees, H. G. Turley; Vegetable Leather, J. S. Rogers; Tannin Analysis, S. W. Stanberry; Hide Powder, I. D. Clarke; Mineral Leather, L. Seligsberger; Physical and Mechanical Properties of Leathers, M. Maeser; Physical Tests, M. Maeser; Sampling, C. W. Mann; Preparatory Tanning Operations, H. B. Merrill; Leather Finishes, C. P. McKee; New Analytical Techniques, E. J. Serfass; Tannery Practices, R. G. Henrich; Industrial Waste Disposal, J. F. Wagoner; Engineering, R. K. Blakely; Standards and Specifications, C. G. Telander; Ways and Means, J. H. Teas.

The Meeting opened Monday morning, June 2nd, with the President's address.

PRESIDENT'S REPORT TO THE ASSOCIATION

By R. M. KOPPENHOEFER

AMERICAN LEATHER CHEMISTS ASSOCIATION

Swampscott, Massachusetts
June 2, 1952

It is a pleasure, at this time, to welcome you to our Forty-Eighth Annual Meeting. It is particularly heartening to see such a large representation of the tanning industry assembled, as we do once each year, to discuss the technical and practical aspects of the business of leather making.

It is the responsibility of the President, at this time, to review the activities of the Association since our last meeting and to present, for your action, any business which should properly come before the full membership. It is also my responsibility to invite members to present any new matters which deserve consideration by the membership and to answer any questions relative to the affairs of the Association over the past twelve months.

TECHNICAL COMMITTEE ACTIVITIES

The most important activity of this or any technical association is the work of the Technical Committees for it is they who provide the tools with which we carry out our assignments. I cannot emphasize this point too strongly for it is my feeling that sufficient numbers of our membership do not recognize this fact. Committee work, as those of you who have served know, is tedious and often unrewarding. Superimposed as it usually is on your daily responsibilities, there is often a tendency to let it slide in preference to problems of more immediate importance. And yet, without a continuing effort on these problems to make certain that our methods are accurate, practical and up-to-date, we would fail in our most important obligation to the industry. There are some of our members who have contributed substantially of their time and their energy in this respect and while their efforts are manifested in our daily work, so unassuming has been their effort that I doubt if many of you know who these men have been and are. I do want to take this opotunity to acknowledge their contributions.

There is much to be gained by participation on one of the Technical Committees. If we analyze the problem we can list the following benefits:

1. The opportunity of contributing in a substantial fashion to the attainment of one of the basic objectives of the Association—the development of accurate analytical techniques.

2. Working in close cooperation with an organized group is an excellent means of getting to know your associates, their problems and their strong points.

3. From committee work you can learn best how the Association functions and what are the broad principles which motivate its policies.

4. Like mathematics in a college curricula, it is a means of sharpening one's technique under the impetus of competition. Better precision and accuracy along with a better understanding of the fundaments of chemistry can be achieved.

5. Finally, as with all Association work, it represents a further schooling in the important techniques of human engineering—the ability to get along with people and to persuade them of your convictions.

Several years ago, in an effort to supply a centralized driving force for all Technical Committee activities, the program was placed under the direction of a Technical Committee Board headed by a chairman who is President-Elect of the Association. This provides the Technical Committees with direct access to Council and supplies a continuity of direction linked to that of the management of the Association. It supplies official recognition to the importance of this work in the affairs of the Association and, on the debit side, places so much responsibility on the President-Elect that his eventual assumption of office is somewhat anti-climatic.

Since last year, one new Technical Committee on Leather Finishes was organized under the direction of Mr. McPhee of International Shoe Company and has begun to function. The Committee on Physical and Mechanical Properties, under Mr. Maeser of United Shoe Machinery Corp., is re-writing all of our methods in this field to incorporate the progress of the last ten years. The group on Mineral Leather under Mr. Seligsberger of Allied Kid Company is a relatively new group which has an extensive program under study. Dr. Merrill of B. D. Eisendrath Company has made notable progress with his group this past year in re-working our techniques for nitrogen and fat analysis. The Vegetable Leather Committee under Dr. Rogers of the U. S. Department of Agriculture is always an active group since the important hide powder assignment, the work on tannin analysis and the determination of hide substance are handled by it. Mr. Wagoner of Armour Leather Company is the new chairman of the Industry Waste Disposal Sub-Committee of the Tannery Practices Committee. And finally, Mr. Telander and his Standards and Specifications Group have done an outstanding job on a difficult and tedious assignment of advising on Government specification problems.

Other Activities

Without attempting to take sides on the matter of whether Korea is a full-scale war, or a police action, Council saw fit, as in World War II, to provide continuing membership for those serving in the military forces.

Recommendations were also made to our Editor relative to certain economies in our Journal. I doubt if many of you have noted that we are using a less expensive paper.

The Association is also in the process of negotiating with the manufacturer of hide powder an agreement which will provide for the continued manufacture of this important laboratory material under any eventuality. Our annual directory has also been expanded and is being issued. A new Methods Book on approved analytical techniques is also being prepared.

Leather Industries of America

Following the announcement by the Tanners' Council of the promotional program on leather, which has been initiated as the Leather Industries of America, Council, with the approval of the Tanners' Council, established an Industry Advisory Committee with Mr. Morrison as chairman. This Committee has not yet started to function in this important assignment. Its purpose will be to provide a source of technical information on any problems which arise during the course of this campaign which has such a bearing on the welfare of the industry.

It is with considerable hesitancy and humility that I, as a representative of the allied trades, dare to add my comments to those which have already been voiced on the objectives of this effort to restore leather to its former position in the demands of the consuming public. My viewpoint must certainly be slanted by my experiences in the petroleum industry. Obviously, the economic factors and the market position which apply to the petroleum industry and their products are not those which apply to the leather industry. One must reason with caution, therefore, in drawing any analogy between the two. Through my early years of association with the leather industry while I was studying and working at their laboratory in Cincinnati, I learned some of the business philosophy of the industry. In more recent years, it has been possible to compare the fundamentals thus acquired with those of the petroleum industry.

One of the most striking differences is the relative position of the technical man—the research chemist and the process engineer—in the two industries. Within the short period of my association of the last eleven years, the technical progress in refining has been so rapid that most refineries have been completely rebuilt in that period. Along with this changing of physical assets, there has been a similar change in manpower assignments. The technical men have moved from the laboratory not only to the plants but more and more they are assuming an increasing responsibility in other sections of the industry such as field engineering, market research and even in direct marketing. Two principles have dominated the trend in the industry which I believe deserve more attention in the leather industry. They are the

continuous operation principle and the mechanization of all processing at the expense of manual labor. While I recognize the leather industry, because of its fundamental assignment, can probably never achieve these objectives to the same degree, yet the economies of continuous operation are so attractive and the costs of labor are increasing at such a rapid rate in recent years that the leather industry must, of necessity, concentrate increasing attention on these principles of processing if leather is going to compete on a price-performance basis with new replacement material. Allow me to remind you that our efforts as technical men have been directed essentially to the chemistry of leather processing and that we have neglected process engineering—or perhaps, I should say, to the neglect of process engineering. In the new program that is being planned as a phase of the Leather Industries of America program, it is my recommendation that this deficiency in our fundamental approach to the problem of leather manufacture be recognized and that one phase of the new program be concerned primarily with process engineering. Since the success of such a program will depend upon the selection of personnel having a broad training in the field of fundamental engineering as well as a wide experience with present practices in the industry, it is my suggestion that the industry be searched to select, perhaps on a loan or part time basis, the most inventive minds to progress this phase of the problem.

There is a second aspect of the technical problem of leather manufacture to which I would like to refer. It has been presented before, in recent meetings, but it deserves restatement. I doubt if there is any single industry in this country which has permitted its technical progress to be dominated by the development of its raw materials suppliers as has the leather industry. Take note that I do not say that the effort of this group has not contributed substantially for there have been significant advances which have come from effort of this character. What is also important is that the process of leather making is such that the processing materials manufacturer needs the assistance of the industry in the development of new ideas and new materials. All industries—ceramics, textiles, paper and rubber, for example—offer similar opportunities for cooperative effort with the chemical industry.

But unlike these industries, there has not been a comparable effort within the leather industry to supplement this program to provide a fund of information or a source of ideas which could supply a self-sufficiency in technical progress and thus effectively safeguard the fundamental interests. This is wrong. You must remember that when a supplier initiates a research project directed to the leather industry it must satisfy two objectives. It must be satisfactory to the leather industry either because of its economics, its simplification of processing or from the increased quality or uniformity of the leather which results therefrom. Secondly, it must fit in with the suppliers' operations in many ways and be attractive economically to him. I believe you will all recognize that this is a sound precept of business administration which

is basic. But what it means, in its most elementary form, is that these developments are first screened before they reach the industry to determine not whether they satisfy the former objective but whether they meet the latter objective. Developments or ideas attractive from a tanners' point of view, as a consequence, may be delayed or may never come to the attention of the industry.

The leather industry need not and should not depend on these sources to the extent that they have in the past. A larger share of the technical progress should originate in the industry laboratories and this can only come from a greater concentration of effort on the part of the industry in this direction. Let's take a completely hypothetical example to illustrate the point. A chemical concern may come across a new organic compound which, in preliminary testing, appears to possess unusual tanning properties. Its development may have been accidental or the result of one of the many projects which are initiated at times in a large organization to cover a development field extensively. Patent investigations may disclose that the particular synthesis has already been covered by a competitor who does not recognize its significance or market research may reveal a disadvantageous raw material supply situation. Under the circumstances, such a development could be shelved as a poor business risk. On the other hand, that same development, if it were made in the leather industry, would not necessarily be subject to the same deterrents and could be progressed normally to its full potentialities. In some industries, and the petroleum industry is an example here, almost the reverse situation applies to developments in the progression of new ideas. By far, the major progress in the field of technology has come from the laboratories of the various segments of the industry. When they have been proved to be practical and the pilot plant studies are complete they are turned over to the outside engineering firms for commercial design and construction. In that manner, the industry is assured that its fundamental interests are safeguarded. It does not preclude or eliminate attractive developments which can and do originate completely with outside organizations that serve the industry in an allied capacity. As with leather, the efforts complement each other but the emphasis is reversed.

The leather industry, while depressed today, still enjoys an enviable position from the standpoint of product quality in the eyes of the consuming public. This is a valuable asset on which to trade and build. I believe the Tanners' Council is moving in the right direction to achieve this objective. The Technical Association of the industry stands willing to do everything within its ability to assist in this program.

The remainder of the program follows:

Monday Morning, June 2

STUDIES CONCERNED WITH THE STRUCTURE OF COLLAGEN.

III. EFFECT OF FORMALDEHYDE TANNAGE UPON THE STRESS-STRAIN BEHAVIOR OF THERMALLY CONTRACTED COLLAGEN.

by N. M. Wiederhorn, G. V. Reardon and Alice R. Browne.

TANNAGE FACTORS AND THEIR EFFECTS ON LEATHER CHARACTERISTICS.

by Wm. B. Zacharias, C. W. Mann, E. T. Steiner and F. C. Horkowitz

DEVELOPMENT OF A FLEX-TENSION TEST FOR LEATHER.

by J. C. Carter and J. R. Kanagy

THE REACTIONS OF FORMALDEHYDE WITH VEGETABLE TANNED LEATHER.

by S. S. Kremen

Monday Afternoon

VEGETABLE TANNINS

by E. S. Flinn and G. W. Stanbery

THE STRUCTURE OF PHLOBATANNINS

by R. C. Putnam, J. C. Rockett and Agnes V. Bowles

CHEMICALLY MODIFIED TANNINS

by K. P. Monroe

THE STRUCTURE OF CHESTNUT TANNIN

by W. R. Browne and R. C. Putnam

TENNESSEE VALLEY OAK BARK AS A SOURCE OF TANNIN

by C. W. Beebe, F. P. Luvisi and M. L. Happich

Tuesday Morning, June 3

ZIRCONIUM TANNAGE—VI: ANALYSIS OF LEATHER CONTAINING ZIRCONIUM

by I. C. Somerville and J. Wendkos

RECENT ADVANCES IN THE THEORY OF THE STRUCTURE OF COLLAGEN AND OTHER FIBROUS PROTEINS

by F. O. Schmitt

THE USE OF CARBON DIOXIDE FOR DELIMING

by E. E. Ochs

APPLICATIONS OF SPECTROPHOTOMETRY AND COLOR MEASUREMENT ON LEATHER

by H. R. Davidson

NOTES ON THE CROCKING OF SUEDE LEATHER

by R. C. Jurney, Jr. and C. H. Geister

Wednesday, Morning, June 4

STUDY OF THE BURST TEST AS APPLIED TO MILITARY UPPER LEATHER

by E. B. Randall, C. W. Mann, J. R. Kanagy and J. Mandel

THE CORRELATION BETWEEN SOME PHYSICAL PROPERTIES OF LEATHER

by W. T. Roddy and R. M. Lollar

NEW ENGLAND TANNERS CLUB, ROUNDTABLE DISCUSSION.

The round table discussion by the New England Tanners' Club, under the leadership of M. Lord, created a lot of interest. It was so favorably regarded that similar discussions will undoubtedly be scheduled for future annual meetings at which time other Tanners' Clubs will be the participants.

Turning to the nontechnical portion of the program, mention will be made of the old fashioned square dance held Monday evening, and scheduled trips to points of historical interest Tuesday afternoon. In addition, the United Shoe Machinery Co. invited Association members to visit its laboratories,

about 150 taking advantage of the invitation. Through K. E. Bell an invitation was extended to visit Lowell Technical Institute, which has established a course in leather technology.

The Golf Tournament was also held Tuesday afternnon. Many participated. Prizes were awarded at the dinner Tuesday evening as follows: Gene Monnier, low gross of 78; Teas Memorial Cup, won by Jim Morrison; Senior Cup, won by Ab Mahoney; Cuthbert Cup, won by H. Stuewe; and Reilly Cup, won by Clint Retsch. Twenty one other players won prizes.

Each year the Convention is favored with an increasing number of wives and daughters of Association members and friends. This year the attendance was especially large. Under the able leadership of Mrs. Maloney, her committee arranged an historical tour of Boston, a boat trip around Boston harbor, trips to Old Salem and Marblehead, golf matches and bridge and canasta.

The Annual Banquet was held Tuesday evening, at which time Lawrence L. Jones, President of Tanners' Council, was the principal speaker. The practical and timely subject of his address was Leather Requires Realistic Research.

Caspar A. Dreuding and Thomas A. Faust, members of the Association since 1905 and 1908 respectively, were made life members.

Joseph R. Kanagy of the National Bureau of Standards received the Alsop Award for the year's outstanding contribution to leather chemistry. The presentation was made by Dr. Highberger.

The election returns showed E. S. Flinn to be the incoming President Elect, and C. A. Ross and F. L. Collins the new members of Council.

H. G. Turley automatically advances to the Presidency of the Association.

The Convention commendably reflected throughout the efforts of the President, his committees, their assistants and the participants in the program.

The Chemistry of Vegetable Tannins

IV. MANGROVE

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HISTORICAL

Mangrove tannin is obtained from various species of Rhizophora. Very little work has been reported on its structure. In 1893 Trimble [1] discussed his examination of extracts of Rhizophora mangle. He found that they had the properties now considered typical of condensed tannins, and he

gave $C_{25}H_{28}O_{11}$ as a possible formula for the tannin. In 1906 Sack [2] reported his work on the American mangrove, Rhizophora mangle, stating that the tannin was obtained by alcohol extraction, followed by precipitation of the phlobaphene by water and then purification by means of the lead salt. He obtained an amorphous red powder to which was assigned the formula $C_{24}H_{26}O_{12}$. From this was prepared a monoacetate melting at 205°C. The tannin gave protocatechuic acid on alkaline fusion. On heating with dilute sulfuric acid he obtained a phlobaphene to which was assigned the formula $C_{45}H_{46}O_{21}$.

No other significant work on the structure of mangrove has been reported. Much work has been done on methods of purification for commercial purposes. To this end Buchanan and others [3] studied dialysis, salt precipitation, solvent methods and hide powder purification.

In summary, mangrove extract has been reported to yield protocatechuic acid on alkaline fusion and to have the formula:

$$C_{25}H_{28}O_{11}$$
$$C_{24}H_{28}O_{11}\ (OH)$$

Purification

Mangrove bark extract is under careful and extensive study in this laboratory so the work reported in this article should be considered preliminary. Only work which has shown some measure of success is discussed. A more extensive purification is in progress than is detailed here; and if continuing analytical agreement is found, this will increase the possibility that the proposed structures are trustworthy.

The mangrove extract being used in the present work is a sample of Borneo Cutch obtained from the Saxe Cutch Corporation of New York.

The crude extract was dissolved in water, extracted with butanol, recovered, dissolved in acetone and precipitated by ether. A seventeen per cent yield of a red, water insoluble, acetone soluble product (A) was obtained. The process was repeated with another sample of crude extract except that a higher concentration in water was employed. The product (B) obtained was cream-white, warm water soluble and acetone soluble. It reddened in light and on standing in a dark bottle. The two products appeared essentially identical when examined by infra-red absorption. It is interesting that merely a change in the concentration of the initial solution resulted in a water soluble product.

Acetylation

The substances obtained were subjected to acetylation and the products analyzed. Substance A corresponded to one of two possible formulas:

$$C_{32}H_{30}O_{12}$$
or $$C_{30}H_{26}O_{12}$$

and its acetyl derivative to

$$C_{32}H_{18}(O\,Ac)_{12}$$

or $$C_{30}H_{14}(O\,Ac)_{12}$$

whereas, product B could be represented by:

$$C_{32}H_{38}O_{12} - 1.5\ H_2O$$

or $$C_{30}H_{26}O_{12} - H_2O$$

and its acetyl derivative by:

$$C_{32}H_{22}O_4(O\,Ac)_8$$

or $$C_{30}H_{18}O_4(O\,Ac)_8$$

The formulas suggested for product A were based in part on a molecular weight of 1,022 found for its acetyl derivative.

Terminal Methyl Groups

A value of 2.77 per cent terminal methyl was found which is in excess of one group for the first formula chosen. Since this determination is not quantitative, it was assumed that two such groups were present. This value was significantly higher than that given by quebracho (1.79 per cent) which was assigned [4] one terminal methyl group. The second set of formulas chosen for mangrove and its derivatives was based on the assumption that the terminal methyl values found represented an impurity and no terminal methyl groups were present.

Acetyl and Keto Groups

Alkaline hydrolysis seemed to indicate the presence of a small proportion of an acetyl group. The infra-red spectrogram, however, indicated only a small proportion of keto function, indeed much less than would be expected for one acetyl group in a compound of the assigned molecular weight.

A purification of another sample of crude extract by an ion exchange resin followed by methyl cellosolve treatment gave a product which showed no keto group at all in its infra-red spectrogram. It is known [5] that some pyrones with terminal methyl groups give acetic acid on hydrolysis. Thus it is possible that the small amount of keto group is due to the partial opening of a flavanol ring with subsequent ketonisation and that the acetyl value is due to the presence or formation of a pyronelike structure.

For comparative purposes the following compounds were analyzed for acetyl content by alkaline hydrolysis:

Compound	Per cent acetyl
Dihydropyran	None
3-Hydroxy flavone	None
Kojic Acid	5.53
	5.48
Fisetin	3.58
	3.60
d-Catechin	7.87 End methyl 0.76

The above data indicate that acetic acid may be obtained by hydrolysis of compounds presumed to be related to phlobatannins without the initial presence of an acetyl or terminal methyl group.

Optical Rotation

It was not found possible to measure the optical rotation of products A and B due to their high absorption, but values were obtained for the acetyl derivatives thus indicating the presence of one or more dissymmetric groupings.

Summary

Evidence has been obtained which points to $C_{32}H_{30}O_{12}$ or $C_{30}H_{26}O_{12}$ as possible empirical formulas for a constituent of mangrove bark extract. Acetyl and methyl derivatives have been prepared.

Experimental

1. *Preparation of Substance A*:

A solution of 60 g. crude Borneo Cutch in 350 ml. water was rotated in a bottle with 350 ml. n-butanol for two hours. Water (300 ml.) was then added, the mixture shaken and the layers separated. The water layer was next shaken with 200 ml. n-butanol. The combined solvent layers were evaporated in vacuo on a water bath. The residue was dissolved in acetone and the solution poured into ether. The reddish precipitate (A) was collected and found to weigh 9.5 g. after drying. It darkened slowly in light, had no melting point, was insoluble in water and ethyl acetate but soluble in acetone.

	Calc.	$C_{32}H_{30}O_{12}$			
	C 63.36	H 4.99	C-Me (2)	4.96	
	Calc.	$C_{30}H_{26}O_{12}$			
	C 62.33	H 4.54			
Found	C 62.90	H 4.85	C-Me	2.77	Ac 5.53 (alkali)
	63.00	4.88			0.00 (acid)
	N 0.26	CH ash	0.37	MeO 2.38	
	0.30		0.45	2.21	

2. *Acetylation of Substance A*:

One and one-half grams of product A was acetylated with acetic anhydride by the usual procedure [4] giving two grams of product. This was then acetylated with acetyl chloride [4] and recovered, then washed with water, methanol, and ether. It was next dissolved in hot methanol, an insoluble portion removed and the final product recovered from solution by chilling. Yield – 0.5 g. On heating it started to darken at 220°C. An X-ray diffraction diagram kindly taken by Dr. R. E. Dreikorn indicated it to be crystalline. There appeared a line in the same position as that found in acetylated quebracho.

	Calc.	$C_{32}H_{18}$	$(OAc)_{12}$	
	C 60.54	H 4.90	MW 1110.9	Ac 46.49
	Calc.	$C_{30}H_{14}$	$(OAc)_{12}$	
	C 59.89	H 4.65	MW 1083	Ac 47.69
Found	C 60.97	H 4.90	MW 1022	Ac 46.19
	61.06	4.98		46.36

Rot. $\left[\alpha\right]_D^{28°C.}$ = +58.7° (0.1583 g. in 13 ml. acetone)

Δ = +0.72°

3. *Preparation of Substance B*:

A solution of 150 g. crude Borneo Cutch in 400 ml. water plus 500 ml. n-butanol was rotated in a bottle for two hours. The layers were separated and the solvent layer evaporated in vacuo on a water bath. The residue was dissolved in acetone, a small amount of insoluble material removed and the acetone solution poured into ether. The precipitate (B) was collected, ether washed, and rapidly transferred to a desiccator. Eighteen grams of cream-colored product having a pink tint were obtained. It was completely soluble in warm water but insoluble in ethyl acetate and benzene. Heat started to darken it at 200°C. The product discolored on standing in a brown bottle.

	Calc.	$C_{32}H_{30}O_{12} - 1.5\ H_2O$				
	C 60.67	H 5.25	C-Me (2)	4.74		
	Calc.	$C_{30}H_{26}O_{12} - H_2O$				
	C 60.40	H 4.73				
Found	C 60.72	H 4.92	C-Me	2.76	Ac	8.29 (alkali)
	60.86	5.08				1.61 (acid)
	N – None		MeO 1.36			1.57 (acid)
	CH Ash – None		1.66			

4. *Acetylation of Substance B*:

Using exactly the same procedure as with product A, 1.7 g. substance B was carried through the two acetylations giving 0.8 g. of white solid having a melting point ca. 190°C.

	Calc.	$C_{32}H_{22}O_4(OAc)_4$			
	C 61.14	H 4.92	Ac 36.52		
	Calc.	$C_{30}H_{18}O_4(OAc)_8$			
	C 60.39	H 4.63	Ac 37.64		
Found	C 61.41	H 4.82	Ac 35.43		
	61.47	4.56	35.69		

$$\text{Rot.} \left[\alpha\right]_D^{27.5°C.} = +49.3° \text{ (0.1583 g. in 13 cc. acetone)}$$

$$\Delta = +0.60°$$

5. *Reacetylation of the Octacetyl Compound*:

The above product was then acetylated again with acetic anhydride. Three-tenths of a gram gave a yield of three-tenths of a gram of light yellow product which was washed with water, alcohol and ether and showed a melting point of 200 – 205°C.

	Calc.	$C_{32}H_{18}(OAc)_{12}$		
	C 60.54	H 4.90	Ac 46.49	
	Calc.	$C_{30}H_{14}(OAc)_{12}$		
	C 59.89	H 4.65	Ac 47.69	
Found	C 60.17	4.68		Ac 48.25
	59.94	4.43		47.83

$$\text{Rot.} \left[\alpha\right]_D^{28°C.} = +57.0°\text{C. (0.1505 g. in 13 cc. acetone)}$$

$$\Delta = +0.66°$$

6. *Methylation*:

Substance B (1.5 g.) was methylated with dimethyl sulfate once in the usual manner and then suspended in ethanol and methylated with diazomethane in ether to give 1.0 g. creamcolored product which had a decomposition temperature of 170°C.

	Calc.	$C_{30}H_{17}O_6(OCH_3)_7 \cdot 2H_2O$				
	C 62.35	H 6.22	MeO 30.48	C-Me	None	
Found	C 61.93	H 6.32	MeO 30.15	C-Me	None	
	62.05	6.02	30.43			

7. *Deacetylation*:

The product of Experiment 2 was deacetylated by refluxing 0.7 g. in 25 ml. ethanol with 2.0 g. potassium acetate for 20 hours. The residue was removed and the filtrate acidified with hydrochloric acid, extracted with ethyl acetate and recovered after drying with sodium sulfate. The product was red-brown and had no melting point.

	Calc.	$C_{30}H_{23}O_9(OAc)_3 - 5H_2O$			
	C 54.41	H 5.33	Ac 16.25		
Found	C 54.53	H 5.18	Ac 15.68	Ash 0.61	

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The Leather Chemist of 1951*

By H. G. TURLEY,

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In 1911 Henry R. Procter, whom we all revere as the Father of Leather Chemistry, wrote a short article for a trade journal—"The Shoe and Leather Reporter"—describing the progress that had been made by the leather chemist during the previous forty years and giving some predictions as to the next forty years. We have now arrived at 1951 and it may be appropriate to discuss the progress made by the leather chemist in the tanning industry, and again hazard a few predictions as to the future.

It must have been true, as Proctor stated, that the progress in leather making, consequent to the industrial revolution, was brought about by mechanical changes. Many machines were invented and leather was produced in a quicker way than by the laborious hand work that had been carried on in making leather since the dawn of recorded time.

It was quite natural, therefore, that the mechanical art should precede the chemical art. In 1911 Procter pointed out that in the immediate future it would be the turn of the chemist in making a contribution to leather technology. As you all know, this is precisely what has occurred. Chemistry, and the chemist, at last made a contribution to the ancient leather industry, with results which are seen on every hand today.

The leather making art proved to be an exceedingly difficult activity to approach from the chemical point of view. It so happened that the industry dealt with the conversion of complex biological materials, hides and skins, by complicated chemical methods involving the natural vegetable tans, animal fats and vegetable dyes and later, complex mineral tanning. Nevertheless, the progress has been sound, sure and, in some cases, spectacular.

*Delivered at the Forty Seventh Annual Meeting, Groton, Conn., June 11, 1951.

Today, the profession of leather chemistry has advanced and there are quite a number of instances where the chemist has become the tanner and manager, or even owner, of a leather making enterprise. Conversely, the skilled tanner today has been forced to become conscious of the chemistry of his business.

Some of the problems that troubled Procter and his colleagues still perplex us today and I shall mention them later on.

However, some of the problems which were so exasperating forty years ago, have been largely cleared up. Taking an outstanding example—the mysterious, puzzling phenomenon of the swelling of hides and skins. The understanding of this has been immeasurably advanced by the concept of measuring the acidity or alkalinity of the tanner's liquors, by the electro potential of the solutions translated in terms of the ionic theory of dissociation into a simple measurement of pH. Procter sensed this and laid the foundation of the understanding of the swelling of gelatin and collagen and mentioned that these electrical measurements were already in use in one of the most progressive tanneries in England. In fact, this was during the pioneering work of Mr. Turney Wood. There has been probably more controversy in the leather industry about the meaning of pH as measured, than any other single idea. As with all new tools, in the early stages of development, it was thought that all tanners' problems would be solved by the application of pH measurement. This, of course, was not so. However, the measurement and understanding of pH has helped greatly in perfecting the technology of leather making. The term, pH, is so commonplace today that a man new to the industry already feels acquainted with pH in a few days' time.

Today, after an evolution through the cumbersome method of determining the pH by the hydrogen electrode with shaky, slow galvanometers, and the quinhydrone electrode, finally the glass electrode has revolutionized the simplicity of the measurement of pH. The glass electrode pH instrument is a marvel of ingenuity and is of tremendous value to the leather chemist. We might say that certain new tanning procedures and bating procedures were made possible by the application of the pH concepts. In the Symposium this morning, there were described new tanning processes whose control is made possible only by attention to the pH measurements of the hides and the liquors.

In 1911 Procter predicted that the day would come when the uncertain, unhygienic bating and puering and drenching processes would be replaced by scientifically controlled substitute materials. This has been a brilliant development in the past forty years, taking bating from the realm of a disgusting, filthy process to a clean, sanitary operation. The fundamental discovery that the bating process was a combined deliming and digestive process resulted in the use of a clean, standardized product. The leather chemist played his part in the improvement of these products and in their application

today. For bating and puering, the tanner today has a choice of many different enzymes, of animal, fish, vegetable and microbiological origin, combined with a choice of several different deliming agents. The tanner can thus produce effects more adaptable to modern leathers than was possible in the past. Nevertheless, the precise and complete function of bating still remains an enigma. It is hoped that in the next forty years sufficient study and progress will be made of this important operation to clarify the still obscure chemistry.

On this occasion, Procter had nothing to say about liming, and, on this subject, we have seen no revolutionary progress. Liming and depilatories are used in much the same way today; however, there has been a better understanding of the role and chemical equivalence of depilatories due to the chemist, so that the effects of the liming of hides and skins is in better control today than when the tanner relied on using old limes containing decomposition matters from previous hides. It was the leather chemist McLaughlin who, reasoning that the old lime liquors contained protein decomposition products of hides, discovered an entirely new type of depilatory material in the amines, among which methylamine is a good example. It was the leather chemist also who expanded the knowledge of inorganic sulfides and their action to the discovery of a whole class of organic sulfides—thio-compounds. It is interesting that whilst no progress has been made in this latter class in the leather industry, the results have been copied with astonishing success in the cosmetic industry for hair waving products and depilatories. Nevertheless, we still do not know the theory on this fundamentally important operation of unhairing. There have been partial theories advanced, but a complete theory must be able to explain not only the mechanism of the action of reducing agents, but also other actions, such as that of the amines and the enzymes.

The chrome tannage has been perfected since Procter's time and is universally used today for all light leathers. The leather chemist has been largely responsible for this. Progress has been made mainly through the application of analytical methods so that the chrome tanner follows the composition of the tanning baths for his leather products, and can manipulate them to produce leathers of desired characteristics, and also economize in the use of his materials. This was forcibly demonstrated in World War II when many tanners were forced to conserve the valuable chromium in their liquor residues and the chemist worked out methods of control. Procter predicted that probably other new mineral tannages would displace chromium and relegate it to a back seat, but it has proved extremely difficult to devise a mineral tannage to substitute readily for the chromium tannage. Chrome tannage, in spite of some drawbacks, is easy to use, rapid, and gives good quality leather. Many mineral tannages have been suggested, such as titanium, tungsten, cerium, molybdenum, and silica, but the only new mineral tannage which has reached a commercial, but very limited success, is that of zir-

conium. In one aspect this tannage has an important advantage over chromium, in that the leather produced is white. The iron tannage which was studied long before Procter's time and abandoned, is even today not successful. Although there is some relationship chemically to the behavior of iron and chromium salts, yet the iron tannage is not satisfactory. Unlike chromium, the oxidative propensity of iron has an unfortunate deteriorating effect on the parent protein of the hide, i. e., collagen. Some tannages of iron, combined with other organic acids, have been moderately successful, but they can hardly be considered as pure iron tannage.

In 1911 the leather chemist was on the threshold of creating for the first time synthetic tanning materials, and although great promise was entertained in the beginning, they remained inadequate and incapable of substituting the natural tans for filling and weight-giving leather properties, but they were valuable auxiliary tanning agents for the production of white, bleached, utility chrome leather and for the bleaching of vegetable leather. However, after much patience and persistence, the leather research chemist finally perfected satisfactory synthetic tanning agents that could produce as satisfactory leather as did the traditional vegetable tans. Some of these products have been thoroughly investigated and proved to make satisfactory heavy and light leathers. In view of the diminishing supply of natural tanning materials, the manufacture of synthetic tanning materials becomes more important than ever. For these products which might well save the leather industry, at some future time, the tanner must thank the research leather chemist.

In the history of leather manufacture, many tannages have been proposed. Many have disappeared under the cold scrutiny of service, economic feasibility, or practical application. Nevertheless, the leather chemist is offering to the tanner today entirely new materials based on startlingly different concepts which may eventually produce quite unusual leathers having special, unique properties that the tanners would never have visualized along classical lines. In this group, we draw attention to the use of synthetic resins and polymeric materials, applied as individual components, as prepared tanning agents, or brought together in situ with the collagen fibers.

The greasing or oiling of leather to render it supple and strong and water resistant is of classical antiquity, but until very recently, tanners, had to rely on the natural animal, fish and vegetable fats. Today the leather chemist can produce synthetic fats capable of replacing these valuable natural fats.

Procter spoke about the use of antiseptics by the tanner, for the preservation of his hides and skins and the control of the liquors. This is quite common today and the tanner can produce mold-proof leathers, preserve his soaking liquors and bating liquors by the use of approved antiseptics—the results of the work of the leather chemist.

Since Procter's time, there has grown up a new chemist, the leather research chemist, devoting himself entirely to the research on leather problems. Today, the leather chemist, to be of real value, must have an unusually wide training. He should be at once a competent and versatile analyst, a good inorganic chemist, a good biochemist, a good organic chemist and, above all, should have or be given the opportunity of acquiring a full training in leather technology. Procter considered the leather chemist would need to have the expensive and wide training comparable to that of a physician and receive the corresponding rewards and social status. For some reason, the leather chemist, in general, has not received this broad training and reward. It is quite possible that this is due to the lack of understanding of the leather industry in the accomplishments of the chemist, or the tanner has relied somewhat too much on the help and advice of outside interests. It is a sad commentary on our industry when we find it being classed as one of the industries spending the least amount of money for research and having no central training school in this country for its technologists, research chemists, and control chemists. May we hope that when the future author of "The Leather Chemists of 2000 A. D." reviews the progress made, he will refer to the contributions of the United States training schools and research institutes for the perfection of leather making. Some sections of the leather industry are now in grave difficulties and substitutes born of the chemical industry have taken the place of leather and we must meet this challenge by a broader research and training program.

With trepidation we shall hazard a few opinions as to the future of leather chemistry. Just as the chemical viewpoint followed the mechanical viewpoint, we believe there will be a growing emphasis on the science of physics. The disposition of the collagen fibers and the effects of various treatments on their swelling and its retention will be increasingly studied. There will be a greater use of physical measurements in order to perfect leather properties, and leather will be sold on its catalog of physical properties. Strength, vapor permeability, water repellency, will not be taken for granted from a small hand test, but will be given a numerical value. In studying some of the aspects of tanning, the services of the electron microscope will be involved. It may be possible to elucidate the tanning mechanism by the use of radioactive tracers and the application of the principles of chromatography. The unhairing theory may be finally explained on a chemical basis and applied with advantage to other industries using keratins. The precise functions of the action of the digestive enzymes will be accurately known and evaluated. Synthetic tans have come a long way and may finally be perfected and more economical processes devised to enable the new tans to compete with, or actually be cheaper than, vegetable materials which will gradually diminish in quantity in time. We should expect to have new mineral tannages and it is hoped that the iron tannage may be finally perfected to be an economical

substitute or alternative to chrome tannage which will be by then more than 100 years old. With some of the at present, unsuspected, and undiscovered chemical development, leather of improved properties suitable for a new age will be designed. Perhaps there will be less leather used in our daily life, but this is a phenomenon which has gone on for more than 20,000 years.

Leather will be substituted by other products, where the use of leather does not take advantages of its unique and aesthetic properties, but I believe leather will be a preferred product and certain of the uses where the appeal to the eye and the appeal to the touch are appreciated will still be desirable in a very mechanical age. If the leather industry successfully fights the inroads made by the synthetic materials, the chemist should reach greater stature and receive greater reward.

Finally, the greater use of statistical methods and better understanding of the expected returns and actual returns from a variable raw stock will be more generally known. Likewise, the planning of experiments for the complicated step-wise process which makes up all leather manufacture will be better laid out and prosecuted, and attention will be given to the statistical planning of the experimental methods.

In conclusion, I should like to repeat Procter's concluding remark, "It is more important to save the life of an industry than that of a millionaire."

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Studies in Unhairing

VI. The Influence of Salts on the Properties of Lime Liquors*

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The liming process has been carefully investigated by many leather chemists since the early studies by Stiasny [1] in 1906, and yet, even today, considerable confusion exists in the literature and among tanners as to the properties of "sharpened" liquors and their influence on skin. The purpose of this work is to correlate some of the available information about the effect of additions of electrolytes to lime liquors in the light of modern physical-chemical theory of solutions. One of the main deterrents to a universal understanding of the properties of these liquors has been the attempt by many investigators to explain lime solubility in terms of the simplified mass action expressions

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ignoring the terms in these expression involving activities. We shall demonstrate that the various mass action expression terms such as solubility product constant and activity coefficient may be used to accurately describe complicated lime liquors provided that they are used in their complete form.

Investigations of liming may, in general, be divided into two broad categories—one of the chemistry of the liquors themselves and the other the effect of these liquors on the skin proteins. The first category is concerned with such factors as the solubility of the lime, the activity of the various ions in solution, the composition of the solid phase, the stoichiometric concentration of the ions present, etc. The second part of the problem is concerned with such factors as swelling of the skin, unhairing, combination of various ions with skin protein, solubilization of skin nitrogen, effect on fiber structure, etc. In this paper, these two phases will be presented separately—first considering the lime liquor chemistry and then proceeding to the effect on the skin.

Stiasny [1] in 1906 studied the effect of additions of various salts to lime slurries and found that:(1) the addition of any salt which formed an insoluble calcium salt caused an increase in the titratable alkalinity of the liquor (i. e. carbonates, oxalates);(2) addition of any salt of high alkalinity produced an increase in titratable alkalinity of the liquor (i. e. Na_2S, NaOH); (3) addition of other salts which are neither highly alkaline nor form insoluble calcium salts also produced an increase in alkalinity of the lime slurry (i. e. NH_4Cl, NaCl, $NaC_2H_3O_2$). In these investigations, Stiasny did not measure the calcium ion concentration, and at that time, methods for estimating the hydroxyl ion activity were not available.

Johnson and Grove [2] in 1931 made a very careful study of the effect of electrolytes on the solubility of lime. Although their experiments were conducted under conditions not found in tannery practice (i. e. pure calcium hydroxide crystals were used and CO_2 was completely excluded from the system) their results are directly applicable to the present problem. They measured the solubility of lime in the presence of increasing concentrations (up to about 4 N) of the alkali and alkaline earth chlorides, the sodium halides, nitrite, nitrate, chlorate, perchlorate, and acetate. Although with the exception of sodium chloride, these salts are not commonly encountered in lime liquors, the general nature of their results makes this work important in our understanding of the lime bath. None of the salts used produced any calcium precipitate and they all may be considered as neutral salts, and yet all produced an increase in the lime solubility up to a certain concentration of added salt and then the calcium hydroxide solubility decreased with further additions. The increase in solubility was not a small effect since, for example, sodium chloride produced a 50 per cent increase while the alkaline earth chlorides (excluding calcium) more than doubled the lime solubility. They explained their results in terms of the Debye-Huckel theory of strong

electrolytes and were able to obtain a quantitative fit of their data curves by means of the Debye-Huckel equation by the addition of one empirical term.

Theis and Ricker[3] in 1940 measured the effect of additions of various sharpeners to lime slurries on both the pH (and thus indirectly the OH ion activity) and the lime solubility. They studied such additives as Na_2S, NaSH, As_2S_3, KCN, Na_2SO_3, $Na_2S_2O_3$, Na_2SO_4, and Na_2CO_3 and NaOH. They found that all salts which produced OH ions in solution either directly or through the precipitation of an insoluble calcium salt decreased the lime solubility and increased the pH (or the OH ion activity) a result to be expected by application of the mass action principle to the solubility product constant. However, they also found that all other salts (i. e.—those which did not produce OH ions in solution either directly or indirectly) increased the lime solubility and decreased the pH slightly, and no reason for this behavior was advanced.

Tomisek[4] made a study in 1947 of the effect of many different substances on the solubility and pH of lime slurries, and his results, in general, were similar to those obtained by Theis and Ricker[3]. In addition to the types of salts reported by Theis, he found that organic compounds such as sugar, albumin, glue, and methyl amine decreased the pH.

Bowes and Kenten[5] in their studies of the effect of salts on lime liquors, observed similar effects to those reported by Theis and Ricker and went on to explain that the lowering of the pH in the presence of NaCl while the lime solubility actually increased, was to be expected in terms of the Debye-Huckel theory.

Experimental

In order that the chemistry of these various liming systems might be more readily understood, it was decided to further pursue the above mentioned investigations by Theis and Ricker and to measure not only the lime solubility and pH of the slurries, but also the titratable alkalinity.

Lime slurries were made up using a commercial lime in excess (3.0 gms. lime per 100 ml.) to which increasing amounts of the various sharpeners were added. These slurries were equilibrated on a shaker for 48 hours at room temperature, and then the pH was measured using a Beckman blue glass electrode calibrated with pH 10 buffer. The slurry was centrifuged to settle the excess lime and aliquots of the clear filtrate taken for analysis. Calcium present was determined by precipitation as the oxalate followed by titration with $KMnO_4$. The titratable alkalinity was determined by titration with HCl to the thymolphthalein endpoint. (Although this endpoint does not allow for titration of all the alkalinity present, most of the true OH ion is titrated whereas most of the buffer salts are not and so this particular endpoint was chosen).

TABLE I

Effect of Various Salts on the pH of Saturated Lime Liquors with No Hide Present

Normality Salt Added	NaCl	Na_2SO_4	$CaCl_2$	NaCN	$Na_2S_2O_3$	Na_2SO_3
0.05	——	——	——	——	——	12.80
0.1	12.46	12.56	12.38	12.59	12.55	13.12
0.2	12.45	12.68	12.29	12.60	12.62	13.35
0.3	——	——	——	——	——	13.44
0.5	12.45	12.85	12.20	12.63	12.64	13.48
1.0	12.46	12.89	11.97	12.67	12.71	13.56
1.5	12.46	12.90	11.84	12.70	12.72	13.61
2.0	——	12.90	11.74	12.72	12.73	——
2.5	——	——	11.60	——	——	——
3.0	——	——	11.42	——	——	——

Grams Salt per 100 ml.	NaOH	Na_2S	NaSH	$Ca(SH)_2$
0.05	12.52	12.50	——	——
0.067	——	——	12.45	12.48
0.10	12.55	12.52	——	——
0.125	——	——	12.49	12.48
0.15	12.60	12.56	——	——
0.20	12.70	12.60	——	——
0.25	12.73	12.63	12.50	12.46
0.375	12.81	12.71	12.52	12.44
0.50	12.91	12.74	12.54	12.41
0.75	12.98	12.82	12.58	12.39
1.00	13.14	12.93	12.60	12.35
1.25	13.19	12.94	12.62	12.31
1.50	——	——	12.62	12.28

The results for various added salts are shown in Tables I-III and are presented graphically in Figures 1-3. These results are in accord with data obtained by previous investigators and we shall proceed, therefore, to an explanation of these various effects in terms of present day physical chemistry.

Measurements of the activity of almost all electrolytes in water solution show, in general, the same characteristics—namely, as the concentration of ions in solution increases the activity coefficient of the electrolyte decreases. The decrease is an almost straight line function of the ionic strength at very low concentrations but levels off as the ionic concentration increases, and finally, at higher concentrations begins to increase again. The theoretical reason for this behavior was presented by Debye and later modified by Huckel and has become known generally as the Debye-Huckel theory of electrolytic solutions[6]. The same characteristic activity curve is obtained

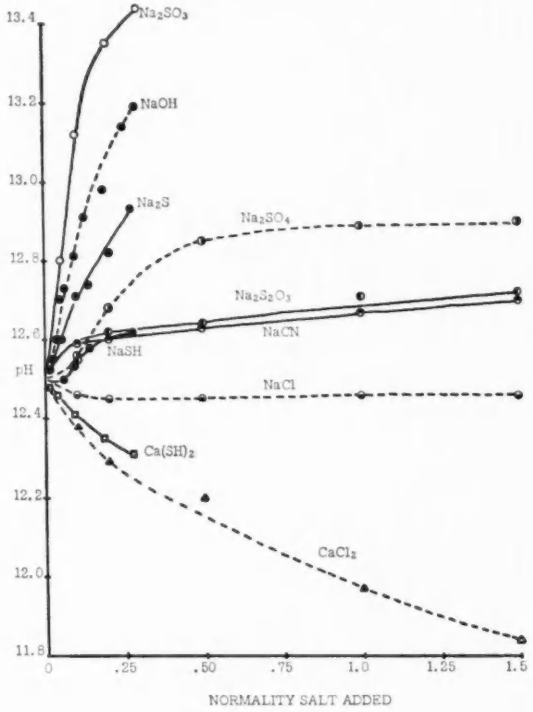

FIGURE 1—Effect of Salts on the pH of Saturated Lime Liquors with No Hide Present. (3.0 grams solid lime per 100 ml. solution).

for a mixture of different electrolytes as is obtained for a single pure electrolyte, thus demonstrating that the effect is concerned more with the total ionic charges present in solution than with the specific ions themselves. An understanding of this principle of ionic activity is essential to an understanding of the lime solution, since the mass action expression for the solubility of lime contains terms in the ionic activities.

The solubility of lime may be expressed thermodynamically as a solubility constant:

$$\text{activity } Ca^{+} \times (\text{activity } OH)^{-2} = SPC \quad \text{or}$$

$$\text{conc } Ca^{++} \times \text{activity coefficient } Ca^{++} \times (\text{conc } OH^{-} \times \text{activity coefficient } OH^{-})^{2} = SPC$$

TABLE II

Effect of Various Salts on the Solubility of Lime in Saturated Lime Liquors with No Hide Present*

Normality Salt Added	NaCl	Na_2SO_4	$CaCl_2$	NaCN	$Na_2S_2O_3$	Na_2SO_3
0.05	——	——	——	——	——	.017
0.1	.060	.058	.145	.052	.053	.005
0.2	.064	.046	.244	.054	.068	.004
0.3	——	——	——	——	——	.004
0.5	.069	.037	.565	.055	.083	.003
1.0	.071	.040	1.09	.046	.092	.002
1.5	.071	.043	1.69	.037	.094	.003
2.0	.069	.046	1.11	.028	.096	——
2.5	——	——	——	——	——	——
3.0	——	——	——	——	——	——

Grams Salt per 100 ml.	NaOH	Na_2S	NaSH	$Ca(SH)_2$
0.05	.040	.042	——	——
0.067	——	——	.050	.059
0.10	.033	.0415	——	——
0.125	——	——	.051	.068
0.15	.026	.041	——	——
0.20	.025	.040	——	——
0.25	.020	.037	.055	.084
0.375	.018	.032	.054	.107
0.50	.014	——	.053	.112
0.75	.010	.023	.056	.144
1.00	.007	.016	.048	.213
1.25	.006	——	——	.240
1.50	——	——	.038	.310

*Expressed as normality Ca++

For very slightly soluble salts such as silver chloride, the activity terms may be replaced by the concentrations of the ions and the result obtained is a close approximation to the truth. However, for a lime solution, the concentration of ions present is too high for this substitution to be made with any degree of accuracy. A further complication arises in lime solutions in that lime does not completely dissociate into calcium and hydroxyl ions, but undergoes secondary ionization as shown

$$Ca(OH)_2 \rightarrow CaOH^+ + OH^- \rightleftarrows Ca^{++} + 2OH^-$$

The dissociation constant for the second ionization has a value of .031 as determined from conductivity data [7].

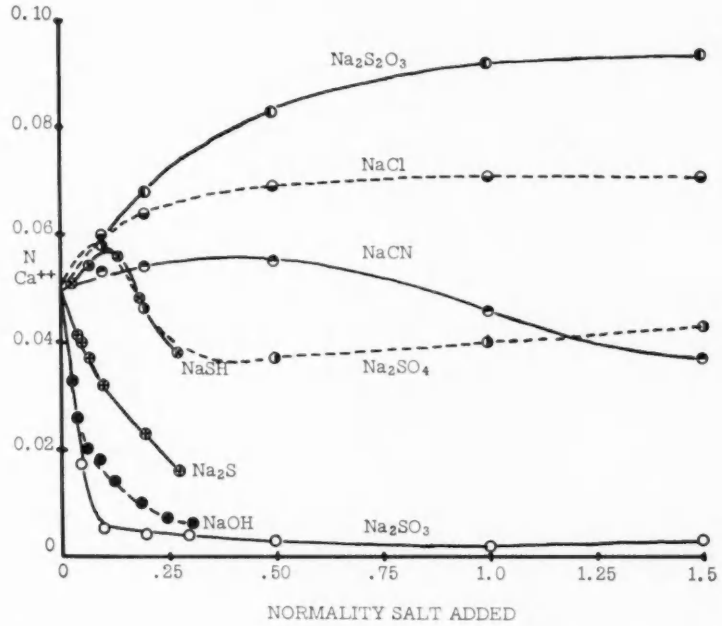

FIGURE 2—Effect of Salts on the Lime Solubility of Saturated Lime Liquors with No Hide Present. (3.0 grams solid lime per 100 ml. solution).

Returning now to the solubility product expression for lime, let us predict what will happen to the stoichiometric lime solubility in the presence of added neutral salts. In the first place, the neutral salt added will increase the total ionic strength of the solution, and as explained above, this causes a decrease in the activity coefficient of both the Ca^{++} and OH^-. Therefore, in order for the solubility product to remain constant the concentration of both Ca^{++} and OH^- must increase in solution. Thus, the predicted result of adding any neutral salt to a lime slurry in that the lime solubility must increase and an examination of the data for NaCl and $Na_2S_2O_3$ in Figure 2 shows that this predicted result actually occurs. Also, from the solubility product expression, we see that the product of the activities must remain constant and if the activity coefficients of both the calcium ion and the hydroxyl ion are affected by the addition of a neutral salt to the same extent then the pH (and thus the OH^- activity) of the solution should remain constant. This is seen to be approximately the case for NaCl in Figure 1.

TABLE III

Effect of Various Salts on the Titratable Alkalinity in Saturated Lime Liquors with No Hide Present*

Normality Salt Added	NaCl	Na_2SO_4	$CaCl_2$	NaCN	$Na_2S_2O_3$	Na_2SO_3
0.05	——	——	——	——	——	.101
0.1	.0545	.060	.034	.052	.059	.168
0.2	.0577	.081	.034	.055	.067	.290
0.3	——	——	——	——	——	.354
0.5	.0640	.123	.035	.064	.079	.359
1.0	.0638	.146	.036	——	.087	.415
1.5	.0634	.164	.043	.082	.090	.435
2.0	.0614	.164	.047	.086	.092	——
2.5	——	——	.054	——	——	——
3.0	——	——	.059	——	——	——

Grams Salt per 100 ml.	NaOH	Na_2S	NaSH	$Ca(SH)_2$
0.05	.049	.048	——	——
0.067	——	——	.044	.042
1.10	.055	.051	——	——
0.125	——	——	.045	.041
0.15	.063	.054	——	——
0.20	.073	.057	——	——
0.25	.078	.063	.048	.038
0.375	.103	.073	.049	.037
0.50	.134	.083	.051	.036
0.75	.194	.110	.053	.036
1.00	.251	.145	.056	.036
1.25	.317	.170	.059	.035
1.50	——	——	.061	.035

*Expressed as normality OH^-

Additions of neutral salts with di- or tri-valent anions should have a greater effect on the lime solubility than additions of NaCl because the higher valence anions increase the ionic strength of the solution more rapidly and, therefore, the activity coefficient of the lime is lowered to a greater degree. (The ionic strength is defined as

$$1/2 \quad \Sigma \quad c_1 z^2_1 \quad + \quad c_2 z_2{}^2 \quad + \quad c_3 z^2_3 \quad + \quad - - -$$

where c is the concentration of each ion and z is its valence. Thus, for 1.0 molar NaCl, the ionic strength is 1.0 whereas for 1 molar $Na_2S_2O_3$ the ionic strength is 3.0). This predicted effect is seen to be borne out by the data for $Na_2S_2O_3$ in Figure 2. However, in this case, the pH also rises (see Fig. 1) with increasing $Na_2S_2O_3$ concentration, an unexpected result in view of the

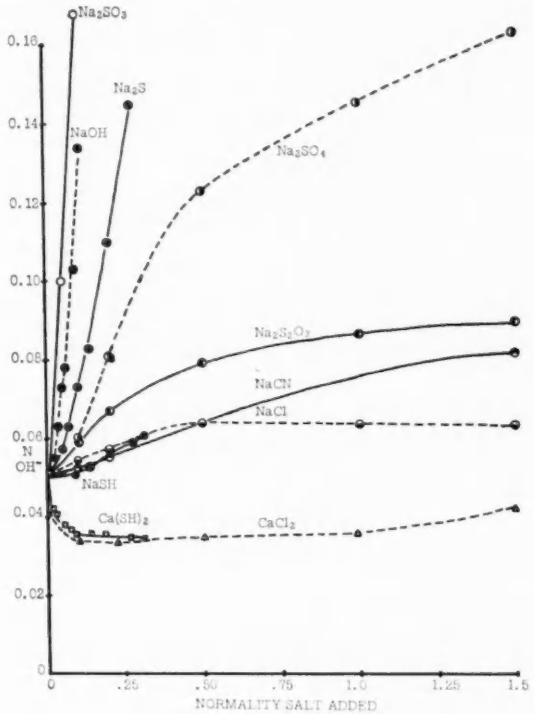

FIGURE 3—Effect of Salts on the Titratable Alkalinity of Saturated Lime Liquors with No Hide Present. (3.0 grams solid lime per 100 ml. solution).

discussion for NaCl and one that requires explanation. This obviously indicates that the activity of the OH^- ion has increased and the activity of the Ca^{++} ion has decreased and may be explained in terms of the secondary dissociation constant for lime. To determine the effect of increasing the lime solubility on this secondary dissociation, it is necessary to solve for the degree of dissociation. The mathematical treatment used is similar to that suggested by Harned and Fitzgerald [8] and is shown in the footnote (1) below. The result of this calculation shows that an increase in the lime solubility forces the dissociation to the left, thus decreasing the stoichiometric ratio of Ca^{++} ions to OH^- ions, and, therefore, the OH^- ion activity (and thus the pH) is increased. There are two factors involved in the dissociation; one the solubility of the lime causing a decrease in the dissociation, and the

other the increased ionic strength (due to added salt) which tends to lower the Ca^{++} ion activity coefficient and thus increase the dissociation. In the case of additions of NaCl, the two factors balance out and the pH remains constant, whereas in the case of the $Na_2S_2O_3$, the solubility is increased more rapidly than the calcium ion activity coefficient is depressed, thus producing an overall effect of increased pH.

(1) The secondary dissociation constant for $Ca(OH)_2$ may be written in terms of the degree of dissociation as follows, assuming that $\gamma\ CaOH^+ = \gamma OH^-$

$$\alpha = 1/2 \left[\sqrt{(1 + m\ \gamma\ Ca^{++})^2 + 4\ m\ \gamma\ Ca^{++}} - (1 + m\ \gamma\ Ca^{++}) \right]$$

where both α the degree of dissociation and $\gamma\ Ca^{++}$ the activity coefficient of Ca^{++} are unknown.

An approximate expression may be written for Ca^{++}:

$$\log\ \gamma\ Ca^{++} \simeq \frac{-2S\sqrt{2\ \mu^1}}{1+A\sqrt{2\ \mu^1}}$$

where μ^1 is the actual ionic strength counting only the number of ions actually present in solution.

$$\mu^1 = (2\ \alpha + 1)\ m$$

Now by assuming a reasonable value for the ionic radius contained in the constant A above (5 Å was chosen since this corresponds closely to the values obtained for other similar electrolytes) it is possible to solve for α by the method of successive approximation. For saturated lime (.022 molar) alone α was calculated to be 0.650, but the calculated α for higher molarities of lime decreased indicating that the dissociation is forced toward the left as the lime solubility increases.

$$Ca(OH)_2 \text{ solid} \rightarrow CaOH^+ + OH^- \rightleftarrows Ca^{++} + 2OH^-$$

The effects which have been previously discussed apply to all strong electrolytes added to lime liquors but in certain cases they are masked by other factors such as the formation of insoluble calcium salts, the addition of hydroxyl ions to the liquor and the hydrolysis reaction of the added salt. The overall effect of adding OH^- ions to the lime slurry may be readily seen by an examination of the NaOH curves in the figures—the calcium ion decreases while both the pH and titratable alkalinity increase. This effect is well known and has been explained by various investigators as being caused by the mass action effect of the added hydroxyl ion on the solubility product of $Ca(OH)_2$. This explanation is undoubtedly true, but too often

the calculation of the magnitude of this effect is made using the simplified form of the solubility product expression (substituting concentrations for activities) and this leads to large errors in the calculated result. For example, the calcium ion concentration as calculated from this simplified solubility product constant expression in the presence of .0938 N[(conc. Ca^{++}) (conc. OH^-) = SPC = 4.27 x 10^{-5}]NaOH should be .004 N. However, the actual calcium ion concentration at this normality of NaOH is .018 N or about 5 times as great as calculated. This fact demonstrates that the effect of "salting in" of lime by electrolytes applies to NaOH as well as to NaCl and $Na_2S_2O_3$ as previously discussed.

Another type of electrolyte commonly found in lime liquors is that which forms an insoluble or partially soluble calcium salt. For example, if sodium carbonate is added to a lime slurry, calcium carbonate is precipitated. There are several common salts of this type and the following equations demonstrate their action:

$$(Ca^{++} + 20H^-) + (2Na^+ + CO_3^=) \rightarrow CaCO_3 \downarrow + 2Na^+ + 20H^-$$

$$(Ca^{++} + 20H^-) + (2Na^+ + SO_4^=) \rightarrow CaSO_4 \downarrow \text{ (partially)} + 2Na^+ + 20H^-$$

$$(Ca^{++} + 20H^-) + (2Na^+ + C_2O_4^=) \rightarrow CaC_2O_4 \downarrow + 2Na^+ + 20H^-$$

$$(Ca^{++} + 20H^-) + (2N1^+ + SO_3^=) \rightarrow CaSO_3 \downarrow + 2Na^+ + 20H^-$$

If the lime was present in large enough excess (as is usually the case in practice) then all the anion of the added salt is precipitated as the calcium salt (except for the small amount still in solution due to the solubility of the particular calcium salts). More lime is then able to dissolve and the final slurry behaves very much the same as a pure lime slurry containing the equivalent amount of NaOH. Since calcium sulfate is soluble to the extent of .03 normal, the addition of Na_2SO_4 to a lime slurry in amounts less than this value produces an effect very similar to $Na_2S_2O_3$ previously discussed. However, additions of Na_2SO_4 greater than .03 N cause a precipitation of $CaSO_4$ and in this region the Na_2SO_4 additions produce an effect similar to addition of an equivalent amount of NaOH.

The third type of salt commonly encountered in commercial liming systems is that which hydrolyzes in water to yield a basic reaction, examples of which are Na_2S, NaSH, and NaCN. The reactions with water which these salts undergo may be written as follows:

(1) $Na_2S \rightarrow 2Na^+ + S^=$; $S^= + H_2O \rightleftarrows HS^- + OH^-$; $K_H = 8.32$

(2) $NaSH \rightarrow Na^+ + SH^-$; $SH^- + H_2O \rightleftarrows H_2S + OH^-$; $K_H = 1.1 \times 10^{-7}$

(3) $NaCN \rightarrow Na^+ + CN^-$; $CN^- + H_2O \rightleftarrows HCN + OH^-$; $K_H = 1.39 \times 10^{-5}$

From the magnitude of the hydrolysis constant of the first of these reactions, it is apparent that this reaction proceeds almost to completion (i. e. to the right) and, therefore, the addition of Na_2S to a lime slurry should have approximately the same effect as the addition of half the amount of NaOH. A comparison of the data for Na_2S and NaOH in Tables I–III shows this prediction to be borne out almost exactly. The reaction with sodium sulfhydrate with water is almost neutral, (as indicated by the hydrolysis constant) and in a lime slurry the reaction would be driven even further to the left by the OH ion from the lime. Therefore, additions of NaSH to a lime liquor should behave almost exactly like additions of NaCl, however, a comparison of the data for the two salts shows that the NaSH acts as a much more alkaline salt than predicted. The most likely reason for this is that the NaSH used for this experiment probably contains a small amount of NaOH as an impurity which caused it to behave more like a mixture of NaSH and NaOH. The NaCN should be more alkaline than NaSH and much less alkaline than the Na_2S according to its hydrolysis constant. The data for this salt confirm this prediction, since both the pH and titratable alkalinity are increased slightly while the lime solubility is decreased slightly.

The expected result of adding a soluble calcium salt to a lime slurry would be a regular decrease in the lime solubility with a resultant decrease in the pH through the mass action effect of calcium ions on the solubility product constant. Additions of both $CaCl_2$ and $Ca(SH)_2$ up to about 0.1 N show this expected result, but above 0.1 N calcium ion added (data for $CaCl_2$ only) the titratable alkalinity begins to increase while the pH continues to decrease. This effect cannot be accounted for as an increase in the lime solubility, since if this were the case the pH would either increase or at least level out. The explanation for this behavior may be the formation of a soluble complex basic salt of calcium chloride as previously suggested by Johnston and Grove [2].

Summary

Modern physical-chemistry theory has been applied to the problem of the effect of salts in lime slurries. It was demonstrated that by employing the principles of interionic attraction (expressed quantitatively as the Debye-Huckel equation for activity coefficient), and the basic principle of mass action (contained in the solubility product constant expression and in the various ionic equilibria expressions such as hydrolysis and dissociation constants) the behavior of lime slurries in the presence of added electrolytes could be satisfactorily predicted.

The general results obtained are tabulated below:

1. A saturated lime liquor with no other salts present contains three types of ions in solution, since the $Ca(OH)_2$ is not completely dissociated. Any

increase in the lime solubility $Ca(OH)_2 \rightleftarrows CaOH^+ + OH^- \rightleftarrows Ca^{++} + 2OH^-$ causes the equilibrium to shift toward the left thus increasing the ratio of OH^- ions to Ca^{++} ions.

2. The addition of any electrolyte to a lime slurry *tends* to increase the solubility of the lime. The higher the valence of either the cation or the anion of the added salt, the greater the magnitude of this effect. This effect is most pronounced at low concentrations of added salt and levels off completely above approximately 1 normal salt concentration.

(a) Monovalent salts (i. e. NaCl, NaSH)—the lime solubility is increased but the pH remains about constant. This is brought about by two effects acting simultaneously; the increased lime solubility tends to shift the lime dissociation to the left (an effect which would increase the pH) while the added ions from the salt tend to force this dissociation to the right and thus the overall effect is to maintain the pH constant.

(b) Polyvalent salts (i. e. $Na_2S_2O_3$, $BaCl_2$) increase the lime solubility to a greater degree than monovalent salts and also cause an increase in the pH. This latter result is caused by a shift in the lime dissociation toward the left, a result of unbalance between the two effects discussed above under monovalent salts.

3. The addition of hydroxyl ions (i. e. NaOH, $Ba(OH)_2$ tends to depress the lime solubility by mass action to a much greater degree than the added ions tend to increase the lime solubility by interionic attraction with the overall result that the calcium hydroxide solubility is decreased while the pH and titratable alkalinity are increased.

4. The addition of salts containing anions which form insoluble calcium salts (i. e. Na_2CO_3, Na_2SO_3, $Na_2C_2O_4$) have the same effect as adding an equivalent amount of NaOH. Those salts which form partially soluble calcium salts (i. e. Na_2SO_4) act in the same manner as other neutral salts up to the limits of solubility of the calcium salt. Additions of the salt beyond this solubility limit produce a result similar to adding NaOH.

5. The addition of salts which hydrolyze in water to give a basic reaction (i. e. Na_2S, NaCN) produce an effect between that of neutral salts and NaOH. The hydrolysis constant of the particular salt determines whether the action is closer to that of caustic or to that of neutral salts. Na_2S behaves almost like half the amount of NaOH whereas NaCN acts more like NaCl.

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Studies in Unhairing

VII. The Influence of Salts Added to Lime Liquors on the Swelling of Animal Skin

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The commercial liming process is carried out primarily to loosen the epidermal tissue and hair of the skin so that they may be readily removed on the unhairing machines. In the course of this unhairing process, however, the skin fibers become swollen and this swelling produces changes in the skin itself which probably affect the characteristics of the finished leather and, for this reason, the tanner desires to control the plumping of the skin in the unhairing bath.

In acid media (i. e. pickling) the degree of swelling may be readily controlled by the addition of salts, but in alkaline media, the effect of added salts has not been as thoroughly investigated. Procter and Wilson [1] in 1916 used the Donnan membrane equilibrium theory to explain the swelling of proteins in acids and alkalies and even today, this concept seems to best explain the experimental data. According to the Donnan theory, acids or bases combine with various polar groups of the protein to form salts and these non-diffusible protein salts cause an unequal distribution of ions inside and outside the fiber which in turn produces an osmotic pressure difference that finally leads to the uptake of water by the fiber. Procter and Wilson added to this concept

by considering that the intermolecular forces between the protein particles resisted this osmotic pressure and Jordan Lloyd[2] in 1920 extended this to include the interweaving of the fibers as a further force resisting swelling. Accordingly, then, the swelling of fibrous proteins may be considered to be a balance between two factors, one the osmotic pressure term tending to increase swelling and the other the structural term tending to prevent swelling. The Donnan theory predicts that monovalent acids and bases will produce a greater swelling than divalent acids and bases, and this has been confirmed by many investigators. A further expected result of the Donnan equilibrium is that with either increasing or decreasing pH from the isoelectric point, the swelling will first increase to some maximum value and then decrease. In acid media, the swelling of both gelatin and collagen follow this expected pattern but the data in alkaline media do not present as clear-cut a picture. Loeb[3] working with gelatin found an indication of a decreased swelling above pH 12, but the effect was not pronounced. Highberger[4] measured the swelling of purified collagen in caustic and also obtained an indication of a maximum swelling point near pH 12. Fritsch[5] in 1938 investigated the effect of both lime and NaOH on calfskin and found definite indications of a maximum in $Ca(OH)_2$, but no maximum in the NaOH. Bowes and Kenten[6] in 1950 have re-investigated the swelling of both purified collagen and gelatin in sodium hydroxide in very carefully controlled experiments. In the case of gelatin, a very definite maximum in swelling was found to occur at pH 12 above which the swelling decreased to pH 13 and then above pH 13 there was a very rapid increase in swelling. With purified collagen, however, no real maximum was found although a plateau in the swelling curve was observed in the region of pH 12-13. Bowes and Kenten explain this apparent discrepancy with the Donnan theory as being caused by the breakdown of protein structural forces with increasing pH. The fact that gelatin follows the Donnan concept even though the magnitude of the swelling of the gelatin is much greater than with collagen would seem to indicate that the protein cohesive forces being destroyed in the case of the collagen must be related to the fibrous structure and the over-all skin structure of the collagen. Stubbings and Theis[7] investigated the layerwise swelling of animal skin and in the grain area they found the swelling curve to follow the Donnan concept almost exactly, passing through a maximum at about pH 12 and then decreasing. However, in the center of the corium they obtained the same type curve as reported by Bowes and Kenten with an apparent plateau in the region of pH 12-13. This lends further evidence to the idea of a breakdown in the structural forces of the skin in alkaline media since in the highly structured area of the grain there is no apparent cohesive breakdown, whereas in the area of large fiber bundles in the center of the corium, breakdown does occur.

The effect of added salts on swelling should be to reduce the swelling according to the Donnan concept, since the difference in concentrations

inside and outside the fiber are reduced by the addition of neutral salt and this has been found to be the case in acid swelling. In alkaline swelling, however, Jordan Lloyd and Pleas [8] found that added salt repressed gelatin swelling up to about pH 10, but above this pH, the swelling was not repressed to the extent expected. Bowes and Kenten [6] found that small concentrations (0.05 M) of NaCl repressed the swelling of collagen in NaOH in the pH range 11-13 by about 10 per cent but that larger additions of NaCl up to 0.5 M produced no further decrease in swelling while still higher concentrations (2.0 M) reduced the swelling still further. Bowes and Kenten [9] also discovered that additions of NaCl to $Ca(OH)_2$ up to 0.05 M increased swelling over the entire pH range from 7-12.5, whereas larger additions up to 0.5 M produced no additional change and concentrations above 0.5 M caused a decrease in swelling. With additions of $CaCl_2$ to $Ca(OH)_2$ the effect of increasing swelling was even more pronounced than with NaCl and the swelling increased progressively up to the highest concentrations tested (1.02 M). That NaCl should cause an increase in swelling in lime solutions might be partially explained in terms of the Donnan concept, since the effect of a monovalent cation on swelling is greater than a divalent cation, but the fact that $CaCl_2$ also causes a large increase in swelling, when, according to the Donnan equilibrium, it should reduce the swelling leads to the conclusion that the divalent Ca^{++} cation must reduce the cohesive forces of the protein tremendously. This divalent cation effect on protein cohesion was suggested by Theis and Steinhardt [10] in 1942 in their interpretation of shrinkage temperature curves for various salts.

Experimental

In this investigation we have restricted ourselves to the study of the effects of added salts in saturated lime slurries since these liquors have the greatest commercial importance. Studies of swelling of animal skin have usually been conducted either on whole pieces of animal skin, (in which case the total swelling is small and therefore small differences in the degree of swelling are difficult to measure) or on ground-up skin material (in which case the structural features of the skin have been destroyed). In order to have a material in which the magnitude of swelling was large and yet one in which the structural features of the skin were retained it was decided to use shredded steer hide (pieces about 1/16" x 1/16" x 6-8") which had been shredded in the salt cured condition for this investigation.

Samples of shredded hide were soaked for 24 hours in water and then placed in saturated lime liquors to which various amounts of salts had been added. The properties of these liquors with no hide present were presented and explained in the previous paper of this series [11]. Liming was done in a hide-liquor ratio of 1:8 for five days with NaCl, Na_2SO_4, $CaCl_2$, NaCN, $Na_2S_2O_3$ and Na_2SO_3 and for two days with NaOH, Na_2S, NaSH and $Ca(SH)_2$.

TABLE I

Effect of Various Salts on the pH of Lime Liquors with Hide Present
(1:8 ratio)

(3 grams solid $Ca(OH)_2$ per 100 ml., 5 day liming)

Normality salt added	NaCl	Na_2SO_4	$CaCl_2$	NaCN	$Na_2S_2O_3$	Na_2SO_3
0.05	——	——	——	——	——	12.55
0.1	12.40	12.37	12.20	12.39	12.45	12.80
0.2	12.40	12.51	12.12	12.42	12.52	13.10
0.3	——	——	——	——	——	13.12
0.5	12.37	12.59	11.98	12.43	12.54	13.13
1.0	12.38	12.83	11.91	12.45	12.65	13.20
1.5	12.37	12.86	——	12.43	12.67	13.26
2.0	12.36	12.86	11.65	12.49	12.68	——
2.5	——	——	11.50	——	——	——
3.0	——	——	——	——	——	——

(1.5 grams $Ca(OH)_2$ per 100 ml.

GRAMS salt per 100 ml.	NaOH	Na_2S	NaSH	$Ca(SH)_2$
0.05	12.30	12.37	——	——
0.067	——	——	12.35	12.33
0.10	12.31	12.38	——	——
0.125	——	——	12.34	12.33
0.15	12.34	12.40	——	——
0.20	12.36	12.48	——	——
0.25	12.38	12.50	——	12.33
0.375	12.42	12.49	12.40	12.32
0.50	12.59	12.53	12.41	12.32
0.75	12.72	12.59	12.45	12.30
1.00	12.92	12.69	12.47	12.29
1.25	13.08	12.78	12.47	12.29
1.50	——	——	12.47	12.28

After liming the samples were drained, carefully blotted and weighed, and the percentage gain in weight based on the salt cured weight was called the per cent swelling. The residual lime liquors were analyzed in the manner previously reported[11] for pH, titratable alkalinity, and calcium and the results so obtained are shown in Tables I-III.

A comparison of these data with those for the same lime liquors with no hide present shows that the presence of hide in the liquor lowers the pH, increases the lime solubility and decreases the titratable alkalinity. These effects may be explained in terms of the nitrogenous material solubilized from the hide in the form of soluble proteins and their degradation products. These nitrogenous materials in solution form slightly dissociated calcium salts and since the total calcium present in solution is measured by the analytical method used, the value reported for calcium includes both the

TABLE II

Effect of Various Salts on the Lime Solubility of Lime Liquors*
(1:8 hide-liquor ratio, 3 grams $Ca(OH)_2$ per 100 ml., 5 day liming).

Normality salt added	NaCl	Na_2SO_4	$CaCl_2$	NaCN	$Na_2S_2O_3$	NaS_2O_2
0.05	——	——	——	——	——	.026
0.1	.070	.071	——	.068	.082	.014
0.2	.077	.062	——	——	——	.004
0.3	——	——	——	——	——	.003
0.5	.086	.047	——	.076	.095	.003
1.0	.091	.042	——	.072	1.09	.002
1.5	.090	.042	——	.059	1.14	.003
2.0	.086	.044	——	.054	1.15	——
2.5	——	——	——	——	——	——

(1.5 grams $Ca(OH)_2$ per 100 ml.)

Grams salt per 100 ml.	NaOH	Na_2S	NaSH	$Ca(SH)_2$
0.0	.058	.059	——	——
0.067	——	——	.063	.073
0.10	.052	.054	——	——
0.125	——	——	.063	.077
0.15	.047	.055	——	——
0.20	.039	——	——	——
0.25	.038	.049	.065	.099
0.375	.030	.047	.070	——
0.50	.024	.043	.071	——
0.75	.016	.029	.059	.185
1.00	.012	.025	.055	.268
1.25	.011	.022	.047	.296
1.50	——	——	.046	.305

*Expressed as normality Ca++

calcium associated with the soluble nitrogenous matter and the free calcium ions. However, the alkalinity reported represents only that which can be titrated to pH 10 (thymolphthalein endpoint) and thus does not include the alkalinity associated with the calcium salts of the soluble nitrogen compounds. Thus while the total calcium in solution is increased in the presence of hide both the "free" alkalinity and the pH are decreased.

The effects of the salts added to the saturated lime liquors on the swelling of the hide is shown in Figure 1. A comparison with the data from Table III indicates a close relationship exists between swelling and titratable alkalinity and this is shown clearly in Figure 2. Over the range of hydroxyl ion concentration of 0.045 N to 0.055 N the swelling is approximately a straight line function of the alkalinity. This relationship may be extremely useful as a

TABLE III

Effect of Various Salts on the Titratable Alkalinity of Lime Liquors*
(1:8 Hide Liquor Ratio, 3 grams solid $Ca(OH)_2$ per 100 ml., 5 day liming)

Normality salt added	NaCl	Na_2SO_4	$CaCl_2$	NaCN	$Na_2S_2O_3$	Na_2SO_3
0.05	—	—	—	—	—	.078
0.1	.048	.058	.042	.054	.059	.155
0.2	.053	.070	.041	.060	.063	.314
0.3	—	—	—	—	—	.324
0.5	.056	.098	.037	.061	.074	.274
1.0	.055	.131	.038	.067	.076	.320
1.5	.052	.136	.044	.079	.078	.301
2.0	.050	.131	.046	.079	.080	—
2.5	—	—	.045	—	—	—
3.0	—	—	—	—	—	—

(1.5 grams $Ca(OH)_2$ per 100 ml.)

Grams salt per 100 ml.	NaOH	Na_2S	NaSH	$Ca(SH)_2$
0.05	.050	.044	—	—
0.067	—	—	.042	.042
0.10	.052	.046	—	—
0.125	—	—	.042	.040
0.15	.055	.047	—	—
0.20	.056	.051	—	—
0.25	.062	.054	.044	.037
0.375	.075	.059	.046	.037
0.50	.091	.066	.047	.037
0.75	.130	.074	.048	.036
1.00	.167	.091	.049	.033
1.25	.210	.111	.049	.035
1.50	—	—	.049	.036

*Expressed as normality OH^-

measure of swelling in practical lime baths containing various salts, and as we shall show later has a greater value for this purpose than the corresponding measurement of pH.

The relation between swelling and pH is shown in Figure 3, and it is immediately apparent that at the same pH value (about 12.4) swelling may vary as much as 100 per cent depending upon the salts present in the liquor, and therefore the use of pH alone in practical control work without a knowledge of the salts present might lead to highly erroneous results.

To explain the close correspondence between swelling and titratable alkalinity it is necessary to consider the factors which produce swelling as postulated by Procter, Jordon Lloyd and others, and to see how these factors are

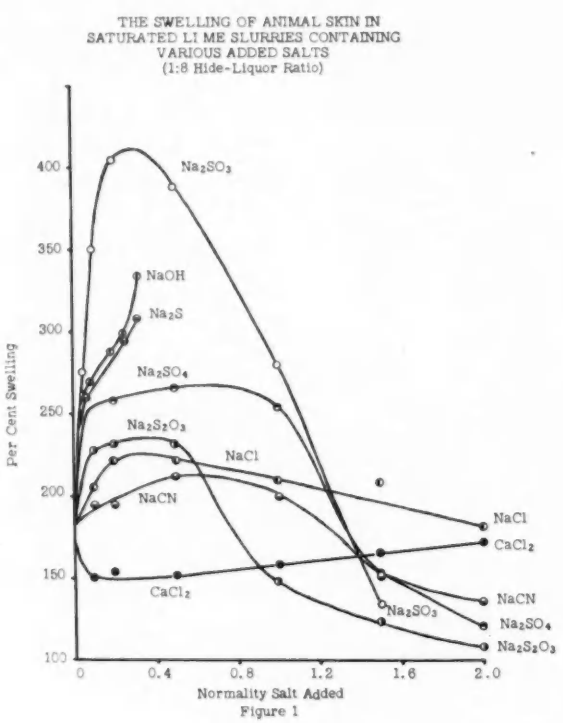

Figure 1

being effected in a saturated lime slurry. One factor influencing swelling is the osmotic pressure (Donnan membrane equilibrium) and as previously discussed this should increase to a maximum with increasing pH (up to about pH 12) and then should decrease. Monovalent bases should produce a greater osmotic term than divalent bases (i.e. NaOH should cause about one-third greater swelling than $Ca(OH)_2$ at pH 12), and the addition of salts with the same cation as the base should reduce the osmotic pressure. Another factor influencing swelling is the breakdown of fiber cohesive forces, and this factor is one which has received little attention and consequently one about which little is known. From the data presented here and from the work of Bowes and Kenton [9] and Theis and Steinhardt [10] it would appear that high alkalinity or long soaking in alkaline liquors causes a breakdown of fiber structure, and that certain cations also cause this condition especially the divalent cations such as Ca^{++} and Ba^{++}.

RELATIONSHIP BETWEEN SWELLING OF HIDE AND TITRATABLE ALKALINITY OF LIME LIQUOR

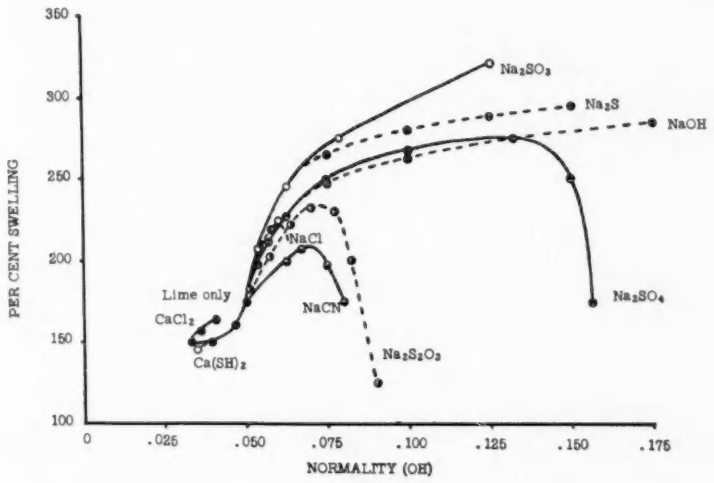

FIGURE 2

Referring again to Figure 3 we see that the addition of any sodium salt in low concentration causes an increase in swelling even though the pH is not altered appreciably. This effect may in the main be ascribed to the effect on the osmotic pressure term caused by the addition of a monovalent cation to the divalent base (an expected Donnan membrane effect). In addition to this main effect a secondary effect occurs as a result of the solubilization of more lime by the added neutral salt. The increased lime solubility means that more Ca^{++} ion is present which can act to reduce the fibrous cohesive forces and thus allow greater swelling. These two effects (increase in osmotic pressure and decrease in cohesive forces) will in general occur for low concentrations of any monovalent salt added to saturated lime liquors.

The addition of $CaCl_2$ to lime produces a decrease in swelling at very low concentrations and then an increase in swelling at higher concentrations. The original decrease is probably due to a combination of the reduction in pH that occurs and the reduction in osmotic pressure that results from the addition of a salt to its base (i.e. $CaCl_2$ to $Ca(OH)_2$). The increased swelling that occurs at higher concentrations of $CaCl_2$ must be attributed to a breakdown of fiber cohesive forces produced by the Ca^{++} ion present.

The addition of NaOH or salts which produced alkalinity either by reaction with lime (such as Na_2SO_4, $NaSO_3$) or by hydrolysis (such as Na_2S,

SWELLING AS A FUNCTION OF pH IN SATURATED LIME SLURRIES WITH VARIOUS ADDED SALTS (1:8 HIDE-LIQUOR RATIO)

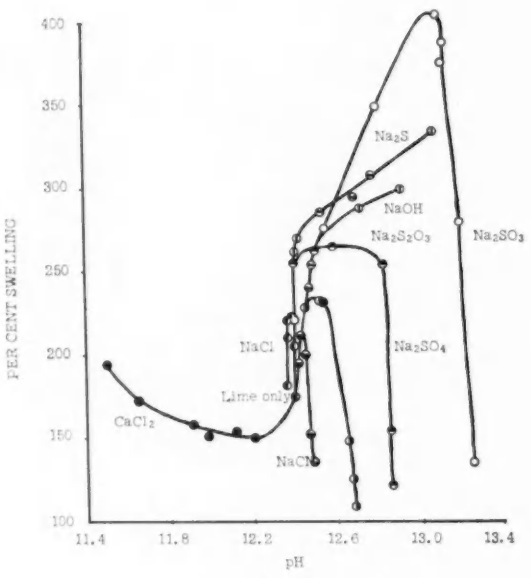

FIGURE 3

NaCN) cause an increase in swelling mostly by an increase in the osmotic pressure term at low concentrations, while at higher concentrations the greatly increased swelling is probably caused by the degradation of the fiber forces. The Na_2SO_3 swelling curve is higher than either the NaOH or Na_2S curves because the hide was in the sulfite liquor for 5 days whereas it was in the caustic liquors for only 2 days.

Higher concentration of added sodium salts (above about 0.2 N) cause an additional effect which results in a drastic reduction in swelling. This effect may be ascribed to a dehydration or in terms of Debye-Huckel theory a change in the activity of the solvent (water). The strong alkalies (i.e. NaOH, Na_2S) were not added in sufficiently high enough concentrations to determine whether this dehydration could also be brought about with these electrolytes, but all other sodium salts added showed the drastic effect produced by dehydration. The concentrations at which this effect became pronounced are

shown in Table IV expressed in various concentration terms common to practice.

TABLE IV

The Necessary Concentrations of Various Salts Added to Saturated Lime Liquors Which Produce Dehydration (1:4 Hide-Liquor Ratio)

Salt Added	Normality	Molarity	Per Cent on Solution	Per Cent on Skin
NaCl	0.5	0.5	2.9	11.6
NaCN	0.5	0.5	2.5	10.0
$Na_2S_2O_3$	0.5	0.25	4.0	16.0
*Na_2SO_4	1.0	0.5	14.2	56.8
*Na_2SO_3	0.5	0.25	3.2	12.8

*The value at which dehydration will occur with sodium sulfate and sodium sulfite is party dependent upon the amount of lime present—(when all the lime has reacted, then the properties of the added salt take effect).

TABLE IV

Effect of Various Salts on Swelling of Hide in Lime Liquors
(1:8 Hide-Liquor Ratio; 3 grams solid $Ca(OH)_2$ per 100 ml., 5 day liming)

Normality salt added	NaCl	Na_2SO_4	$CaCl_2$	NaCN	$Na_2S_2O_3$	Na_2SO_3
0.05	——	——	——	——	——	276
0.1	206	256	150	195	228	350
0.2	221	258	154	195	232	405
0.3	——	——	——	——	——	376
0.5	221	266	152	212	232	388
1.0	210	254	158	200	148	280
1.5	209	153	166	152	124	134
2.0	181	121	172	136	108	——
2.5	——	——	194	——	——	——
3.0	——	——	——	——	——	——

(1.5 grams $Ca(OH)_2$ per 100 ml.)

Grams salt per 100 ml.	NaOH	Na_2S	NaSH	$Ca(SH)_2$
0.05	202	222	——	——
0.067	——	——	188	170
0.10	198	220	——	——
0.125	——	——	180	160
0.15	222	228	——	——
0.20	222	240	——	——
0.25	262	260	197	160
0.375	270	256	213	155
0.50	269	286	220	170
0.75	288	256	220	154
1.00	300	295	220	143
1.25	334	308	225	152
1.50	——	——	224	145

Most commercial lime liquors will be lower in salt content than the values shown in Table IV, and so the dehydration effect would not be expected to take place in present practice. However, the important value is not so much the amounts of each individual salt present as the total amount of salts present, since if this exceeds about 0.5 N the dehydration effect will begin to occur. It is possible that this salt effect could be used in practice to decrease and control swelling, but no information as to the value of such control is available at present.

Summary

The measurement of swelling of animal skin in saturated lime liquors containing various concentrations of added salts including NaCl, NaCN, NaSH, $Na_2S_2O_3$, Na_2SO_4, Na_2SO_3, NaOH, Na_2S, and $CaCl_2$ has been made.

The results show that over a limited range of hydroxyl ion concentration (0.045 N to 0.055 N) the swelling of the skin is almost a linear function of the hydroxyl ion concentration.

The addition of any sodium salt in low concentrations produces an increase in swelling, and the addition of a calcium salt produces a decrease in swelling. The addition of high concentrations of neutral sodium salts produces a drastic decrease in swelling and the addition of high concentrations of a calcium salt produces increases in swelling.

An explanation for the effect of various salts added to lime liquors on the swelling produced in the skin was made on the basis that swelling is a result of three fundamental factors—osmotic swelling or Donnan membrane effect, change in the fiber cohesion, and dehydration.

The results obtained suggest several practical applications in tannery beam house operations:

1. Control of lime liquors by means of pH measurements alone is unreliable, and a measurement of titratable alkalinity on the centrifuged liquor (to pH 10) would be more reliable.

2. Sodium salts may be used to increase swelling in the liming operation where this condition is desired.

3. High concentrations of sodium salts might be used to decrease swelling in the liming operation where this condition is desirable.

Acknowledgment

The authors take pleasure in thanking the Pfister and Vogel Tanning Company, S. B. Foot Tanning Company, Ohio Leather Company, Albert Trostel and Sons Company, A. F. Gallun and Sons Corporation, Fred Rueping Leather Company, and Seton Leather Company for active support and encouragement in the prosecution of the studies given herein.

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Formate Chemistry and its Application to the Deliming, Pickling, Depickling, Tanning and Neutralization of Chrome Leather. I and II.*

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I. INTRODUCTION

Many tanners have concluded that the addition of the formate radical to the various chrome tanning processes, such as deliming, pickling, depickling, tanning and neutralizing, either facilitate the processes or contribute new properties of commercial value to the resulting leathers.

The application of the formates to the tanning processes as reported by Theis[1] and others are varied, both as to materials, amounts used and points of application. So it would seem that an understanding of the chemistry of the formates, which is simply the chemistry of a weak acid and its salts, would aid in understanding these applications. There are three chemical combinations of the formate radical available commercially. These along with related chemicals are described in Table I.

The only material in Table I containing active impurities is sodium formate. These impurities are not a deterrent to the tannery use of the material. The oxalate is known to have an effect on tanning reactions, but the amount present is negligible. The amount of alkali present (principally sodium carbonate) is appreciable, but this can be compensated for whenever desirable. As long as 25 years ago the use of sodium formate was considered as a neutralizing agent. This application met with indifferent success. While the recent work of Theis has given a tremendous impetus to the use of formates, the emphasis has been on adding the formates to the chrome liquor.

*Presented at the Forty Seventh Annual Meeting, Groton, Conn., June 12, 1951.

TABLE I

Chemical Name	Formula	Formula Wt. (1934)	Usual Commercial Purity	Description	Other Active Ingredients	*Cost per lb. $
Formic Acid	HCO_2H	46.02	90%	Colorless liq. in water sol.	None	.20
Sodium Formate	$NaCO_2H$	68.00	96%	White powder	NaOH Na_2CO_3 $Na_2C_2O_4$	.068
Calcium Formate	$Ca(CO_2H)_2$	130.10	99.5%	Gray powder	None	.056
Sulfuric Acid	H_2SO_4	98.08	93.2%	Colorless liq. in water sol. 66° Be	None	.011

*In carload quantities at Chicago, May, 1951.

In the discussion at Lake George [2] there seemed to be an underlying recognition that the use of the formate salt resulted in the substitution of formic acid for sulfuric acid. Theis, Thorstensen and Agarwal [3] show the replacement of sulfuric acid by formic acid when adding sodium formate to chromium sulfate liquors. Stumpf [4], in his formula for bating, pickling and tanning of chrome side leather in one continuous operation, which he states has produced excellent leather in a number of tanneries, introduces the formate into the pickle solution with the salt (sodium chloride) prior to the addition of the sulfuric acid and he clearly recognizes the formation of the formic acid. This appears to be complete recognition of the chemical transformations involved, and that is, whenever the salt of a weak acid and a strong base are introduced into a strong acid medium, such as a sulfuric acid pickle or an acid chromium sulfate solution, the salt immediately liberates the weak acid, and the strong base combines with the strong acid. This does indeed have a pseudo neutralizing effect. There is an immediate rise in the pH value, because formate molecules replace sulfuric acid molecules with formic acid molecules. This is particularly significant in the case of chrome tan liquors because the net effect is an increase in pH without a change in basicity as defined by Schorlemmer. There is also a resulting increase in the solubility of one of the reaction products when the formate chrome liquor is used to pickle-tan partially delimed stock. The reaction product is the soluble calcium formate in place of the relatively insoluble calcium sulfate.

Figure I shows the relations between the pH values of formic and sulfuric acid in chemically equivalent solutions, and indicates that the substitution of formic acid for sulfuric acid will increase the pH from 0.5 to 1.5 pH units, depending on the pH level at which the transformation takes place. The authors expect to show that formates have specific applications to each of the related processes—deliming, pickling, depickling, tanning and neutralizing—but since the reactions involved in pickling are clear cut and since

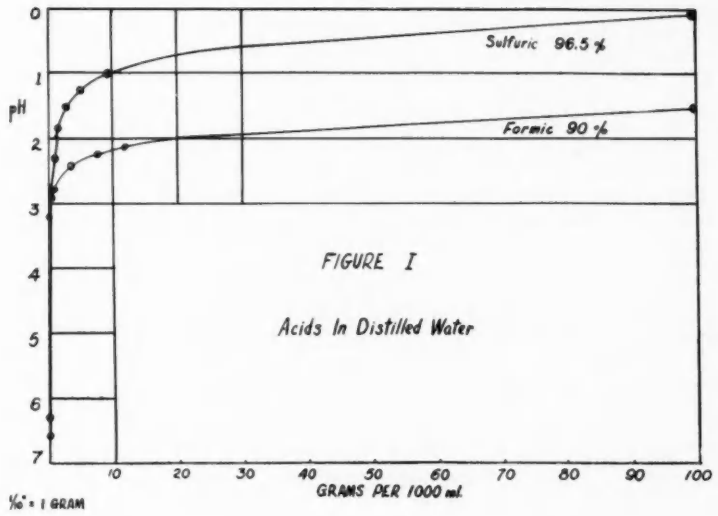


FIGURE I

Acids In Distilled Water

pickling and deliming are frequently done together and are first in the order of procedure, these are considered first.

II. Deliming and Pickling

Chemically speaking, the simplest thing to do would be to use formic acid and sodium chloride. However, at present market values the following equations show that either of the formate salts, when used with sulfuric acid, is a cheaper source of formic acid. The equations show the materials used in stoichiometric proportions. The formula weights and purities are from Table I.

1. SODIUM FORMATE

2 $NaCO_2H$	plus	H_2SO_4	→	$2HCO_2H$	plus	Na_2SO_4
2 x 68.0		98.08		2 x 46.02		142.05
.96		.932		.90		1.00

Thus 141.7 lbs. sodium formate plus 105.2 lbs. sulfuric acid give 102.3 lbs. formic acid and 142 lbs. sodium sulphate—or 138.5 lbs. sodium formate plus 102.8 lbs. sulfuric acid give 100 lbs. formic acid (90 per cent).

2. CALCIUM FORMATE

$Ca(CO_2H)_2$	plus	H_2SO_4	→	$2HCO_2H$	plus	$CaSO_4$
130.1		98.08		2 x 46.02		136.14
.995		.932		.90		1.00

Thus 130.8 lbs. calcium formate plus 105.2 lbs. sulfuric acid give 102.3 lbs. formic acid plus 136.1 lbs. calcium sulfate. Or 127.9 lbs. calcium formate plus 102.8 lbs. sulfuric acid give 100 lbs. formic acid (90 per cent). It can be seen from the above equations and Table I that the cost of 100 lbs. of formic acid will vary according to the commercial source.

TABLE II

Cost of 100 lbs. of 90 per cent formic acid when derived from various commercial sources:

From formic acid: 100 pounds, 90 per cent formic acid		$20.00
From sodium formate and sulfuric acid:		
137.6 lbs. sodium formate	9.42	
102.8 lbs. sulfuric acid	1.13	10.55
From calcium formate and sulfuric acid:		
127.9 lbs. calcium formate	7.16	
102.8 lbs. sulfuric acid	1.13	8.29

It would appear that these materials could be used interchangeably and that cost, availability, and convenience will decide which is to be used. Of course the formation and effects of the by-products of the reactions must be considered. There will be processes where the calcium sulfate will have a noticeable effect and others where it will be the sodium sulfate. In either case some adjustment may be made. Part of the calcium sulfate can be removed by decantation or filtration and the sodium sulfate and soluble $CaSO_4$ may be compensated for by the addition of less salts, either chlorides or sulfates.

Laboratory Pickle Experiments

Experiments were set up to test the validity of the above conclusions. The experiments were all run on commercially bated completely delimed cattle hides with a sulfuric acid pickle, in comparison with various formate combinations with and without sulfuric acid.

The control formula was:

500 grams drained bated stock
200 per cent water (1000 ml)
12 per cent salt (60 grams)
2 per cent sulfuric acid (10 grams—10.4 g. 96.5 per cent acid)

TABLE III

Composition of Pickle Solutions

Test No.		5	6	7	8	9	10	12	14	15	16	17	18
						Grams							
Water		1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Sodium Chloride 100 Per Cent		60	60	60	60	60	60	60	60	60	60	60	60
Sulfuric Acid 96.5 Per cent		10.4	10.40 .02 .49 10.91	10.4	——	10.4	——	17.6	7.5	10.4	10.4	——	——
Formic Acid 90 Per cent		——	——	——	10.4	——	10.4	——	——	——	——	49.4	——
Sodium Formate 100 Per cent		13.8	——	——	——	——	——	——	——	——	——	——	——
Sodium Formate NaCOOH	95.23												
NaOH	.11	——	14.5	——	——	——	——	——	——	——	14.5	——	——
Na_2CO_3	3.50												
$Na_2C_2O_4$	.47												
Calcium Formate 99.5 Per cent	——	——	13.2	——	——	——	13.2 b plus 3.0	——	13.2	——	——	——	——
Sodium Sulfate 100 Per cent	——	——	14.3	——	——	——	——	——	——	——	——	——	——
Hydrochloric Acid 37 Per cent	——	——	——	——	——	——	——	——	——	——	——	——	20.1

TABLE IV

Test No.	5	6	7	8	9	10	12-12b	14	15	16	17	18
Description	NaF	NaF	CaF	HF	H_2SO_4	HF	CaF	H_2SO_4	CaF	NaF	HF	H Cl
Note	1	2	3			4	5					
Time – Hours	pH Values											
0	2.30	2.02	2.20	2.08	0.84	2.08	1.09	0.93	2.10	2.32	1.78	0.75
.50							1.48	1.42	2.63	2.81	2.19	
.75	2.82	2.71	2.80	2.80		2.09						1.04
1.25					1.32							
1.50	3.00	2.91	2.99	2.98		2.08						
1.75					1.42				2.99	3.10	2.42	1.35
2.33							1.93	1.90				
3.50							2.11	2.14				
5.50												
6.25	3.30	3.27	3.30	3.30	1.70	2.08						
20.00	3.50	3.41	3.48	3.49	1.74	2.06	2.40	2.60	3.38	3.46	2.60	1.46
	Titrations—see Note 6											
0				18.3	17.8		30.3	12.8	19.6	19.0	65.6	20.4
*20				6.5	3.5		15.5	2.8	7.2	6.6	45.0	4.4
	Per cent Take Up—see Note 7											
*20				64	80		48	82	63	65	31	78

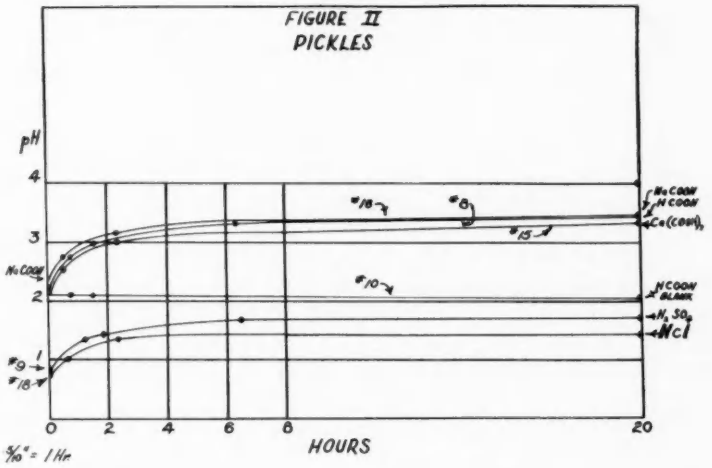
Note: F as used above represents COOH (Formate).

1 – C. P.
2 – Commercial: adjusted for alkalies.
3 – Sodium sulfate added.
4 – Blank.
5 – Stumpf formula.
6 – 10 ml. titrated with N/10 NaOH and phenolphthalein.
7 – Includes acid in liquor held by stock.
* – Tests 12b, 14, and 17 – Take up at 44 hours.

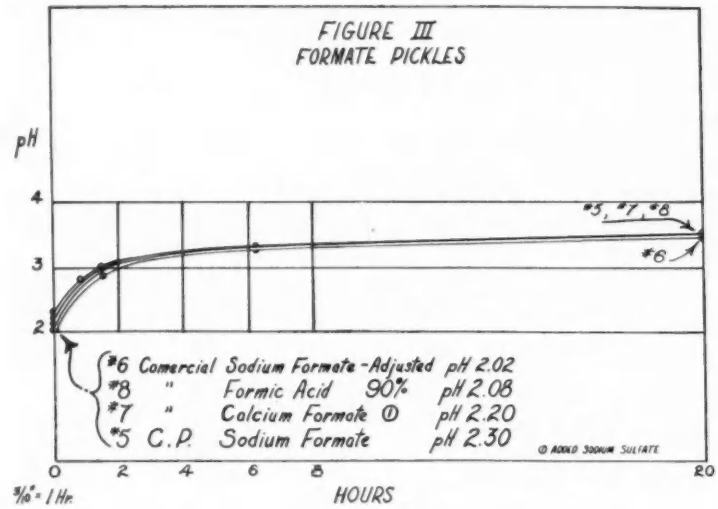
This conforms to the general pattern of a commercial paddle pickle. All tests were run at 75-80°F. The stoichiometric amounts of the materials used are shown in Table III.

The bated stock was added to the prepared liquors, then stirred continuously for 1.5 hours, and intermittently thereafter. The course of the pickling reaction was followed by taking pH values of the liquor as indicated in Table IV. These results are shown graphically in Figures II, III and IV.

In Figure II we have a sulfuric acid pickle, a hydrochloric acid pickle and three formate pickles,—one with formic acid and two where the acid is obtained by the reaction between the formate salts and sulfuric acid.



The similarity of the formate pickles and their divergence as a group from the sulfuric and hydrochloric acid pickles are striking. Since calcium sulfate is precipitated when calcium formate and sulfuric acid are mixed, we have positive evidence that formic acid must be formed in this reaction; and despite the incomplete precipitation of the calcium sulfate, the pH values indicate that the formic acid reaction is complete. For example, No. 8, the formic acid pickle, has an initial pH of 2.08; and No. 15, the calcium formate sulfuric acid pickle has a pH of 2.10. The higher pH 2.32 of the sodium formate pickle No. 16 might indicate less than complete formation of formic acid. However, this higher pH can be attributed to the alkalies known to be present. That this is true is substantiated by No. 6 shown in Fig. III where the alkalies were compensated for by the addition of extra sulfuric acid, with a resulting pH of 2.02.



Test No. 10, a formic acid blank run under the same condition as No. 8—in an open vessel with agitation—is introduced to show that there is no increase in pH due to loss of formic acid to the atmosphere during a formic acid pickle run. The fact that formic acid is a low boiling liquid 100.8°C and in 90 per cent solution has partial pressures as follows—50°C.-12.4 mm Hg., 86° -37.2 mm and 104° -59.1 mm [5]—may lead us to suspect such a loss. However, this test clearly indicates that no such loss occurs. Actually more water than formic acid is lost from dilute solutions. Figure III shows the comparison of formic acid, with three other formate tests; No. 5, C. P. sodium formate: No. 6 commercial sodium formate (when the contaminating alkalies are compensated for); and No. 7 calcium formate (when the amount of sodium formate produced in the sodium formate pickle is added to the calcium formate pickel). Here the convergence is even more striking than in Figure II. The agreement between the calcium formate and the sodium formate pickle indicates that the amount of calcium sulfate precipitated from the calcium formate pickle is not related to the amount of formic acid formed.

In these pickle tests the pH was stabilized immediately while the calcium sulfate was precipitated over a period of 30 to 40 minutes. The amount of calcium sulfate which precipitates as $CaSO_4.2H_2O$ (gypsum) [7] remaining in solution can vary from nearly 0 to 100 per cent. While it is but slightly soluble in water, it is more soluble in sulfuric acid and much more soluble in formic acid. While the varying solubility does not affect the amount of formic acid

formed under these pickling conditions, the presence of the calcium sulfate might have effects on subsequent processes and leather properties.

Some of these pickle liquors were titrated with sodium hydroxide and phenolphthalein at the beginning and the end of the tests to show the actual takeup of acid. The results are shown in Tables IV and V. This indicates that, when stoichiometric equivalents are used, sulfuric acid (Test 9) with its greater ionic activity has a greater affinity for hide substance than does formic acid (Test 8). Furthermore, the results are the same as in Test 8 when the formic acid is derived from either calcium formate (Test 15) or sodium formate (Test 16).

TABLE V

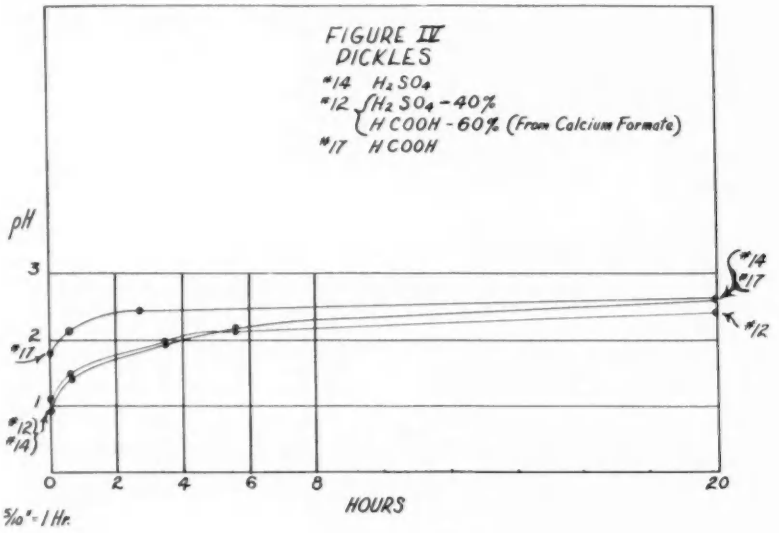
Test No.	Chemical Equivalents		Per Cent Acid	Acid Taken Up
	Sulfuric Acid	Formic Acid	Taken Up	Equivalents*
14	.72		82	.59
15		1**	63	.63
8		1	64	.64
16		1***	65	.65
9	1		80	.80
12b	.442	1.225	48	.80
17		4.75	31	1.47

*Includes acid in solution in water held by stock.
**From calcium formate.
***From sodium formate.

Steiglitz[8] gives the relative acidic activities as hydrochloric 100, sulfuric 74 and formic 1.3. Calculated from Lange's[9] ionization constants sulfuric acid is 89 and formic acid is 1. However, Figure I shows that to gain pH 2.0 requires only 30 times the amount of formic acid that would be required by sulfuric acid. Tests No. 17 and No. 14 (discussed later) show that it requires only about 6.5 times more formic acid than sulfuric to arrive at the same pH in pickled stock.

This lower affinity of formic acid would indicate that a straight formic acid pickle might not be satisfactory commercially. If we examine the Stumpf formula[4] we find that an excess of sulfuric acid is used. The 40 lbs. of sulfuric acid with the 30 lbs. of calcium formate represents an excess of 69 per cent over the amount required to convert the calcium formate to formic acid. Actually the pickle is 60 per cent formic and 40 per cent sulfuric acid. This combination has both the high ionic acitivity of sulfuric acid and also the specific chemical activity of the formate radical. Another set of pickle tests was set up: No. 12, using the same amount of calcium formate as No. 7 but using the same excess sulfuric acid as in the Stumpf formula. In terms of the prior pickle test this is 1 equivalent of formic acid and .69 equivalents of

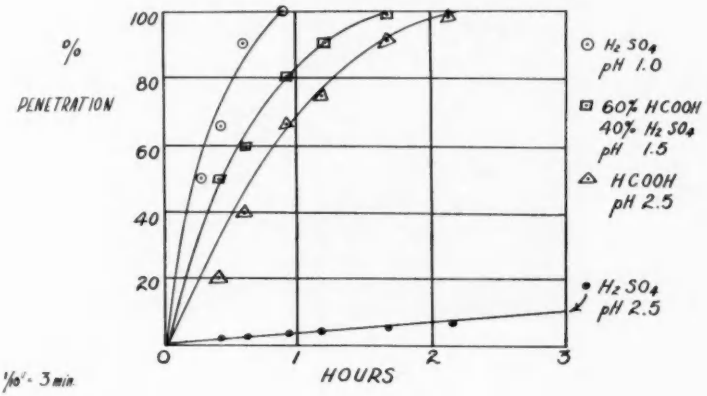
sulfuric acid. Test No. 14 was made with .72 equivalents of sulfuric and No. 17 with 4.75 equivalents of formic acid. These were designed to have similar pH values, and the results are shown graphically in Figure IV. The curves of No. 12 and No. 14 are nearly identical. Reference to Figure I shows that the initial pH values (approximately 1.0) of No. 12 and No. 14 are unobtainable with formic acid alone. This is borne out by the higher initial pH value of No. 17—1.78; but the final pH of No. 17 is identical with No. 14.



Three grams calcium formate were then added to No. 12 reducing the excess sulfuric acid to .35 per cent or .44 equivalents, increasing the formic acid to 1.22 equivalents and raising the pH. The pH value 24 hours later was 2.76. In the meantime in No. 14 the pH had increased to 2.80 and No. 17 to 2.71. From this set of tests, Figure IV, we see that we can arrive at approximately the same pH value in pickled stock by using either .75 equivalents sulfuric acid, .50 equivalents sulfuric acid and 1.25 equivalents formic acid or 4.75 equivalents formic acid alone. These liquors were then titrated to determine the amounts of acid taken up. See Tables IV and V. We find that the low sulfuric acid pickle No. 14 has a high percentage takeup but is low in equivalents taken up. The high formic acid pickle No. 17 has a low percentage takeup, but due to the high chemical concentration the equivalents taken up are high. The mixed pickle No. 12 gives a low percentage takeup but the equivalents taken up are identical to the normal (1 equivalent) sulfuric acid pickle.

While we have not determined the relative amounts of the two acids taken up, since we used only .44 equivalents of sulfuric with a total of .8 equivalents of acid taken up, it would appear that the ratio is probably in the order of 50/50.

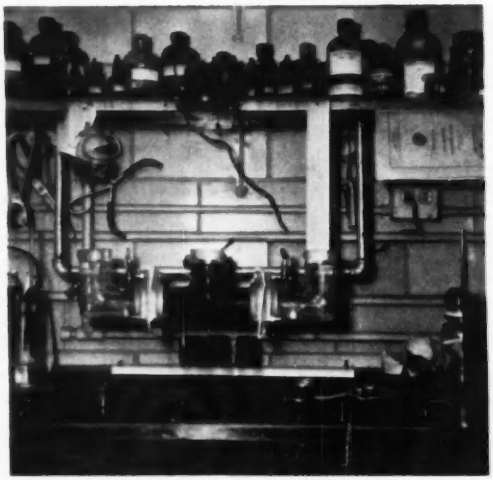
FIGURE V
PICKLES



RATE OF PENETRATION OF PICKLES

Since one of the claims made for the use of formates is the reduction in processing time, we have developed an apparatus to measure penetration times as affected by chemicals, concentrations, pH values, temperatures, etc. (See Figure VI). This is a modification of an apparatus described by Strandine, DeBeukelair, and Werner[10]. The apparatus is simple, consisting of 3 pieces of standard Pyrex glass pipe of 2" diameter. One tee and two 90° els. These are joined together with aluminum flanges. The test pieces serve as gaskets and completely separate the liquids in the els from the liquid in the tee. The center or tee section holds approximately 500 mls, and the el ends each hold 325 mls. The portion of an 8 oz. thick test piece in contact with the liquids will weigh approximately 10 grams. Due to the large volume of solution in relation to the weight of the test piece, the changes in concentration during a test are very slight. The test piece is maintained in equilibrium with the preparatory liquor until it is penetrated by the test liquor. Two tests may be run simultaneously by putting the preparatory liquor in the center section and the test solutions in the els. Or a duplicate test can be run by putting the test solution in the tee and the preparatory liquor in the els. Considerable variation in the design could be had by using other standard parts

FIGURE VI



H-R PENETROMETER

that are available. Whole hide may be used for test pieces, and penetration may be measured from grain to flesh or from flesh to grain. In this series of tests plump steer hides 12-14 oz. thick were selected after unhairing. 10″ strips were cut along the backbone and these were split down to 8.5 oz. by first removing 2 to 4 ounces from the flesh side and then 2 ounces from the grain side. These strips were refrigerated and prepared for testing as required.

Many ways of determining the completion of penetration may be devised. In these pickle tests the face of the specimen away from the test solution was swabbed with an indicator, such as brom cresol green. When the solution on one side of the specimen is colored, as with a chrome liquor, and the other is not, as with a pickle, the migration of color into the colorless phase is readily detected.

Penetration Tests, Series No. 1

This series was run in the conventional manner, i. e., penetration was from both sides into the center. Penetration was measured by making cuts and applying indicators at intervals. There was some agitation. Split test pieces of approximately 40 grams each were used after deliming and washing. The makeup of the test solutions and results are shown in Table VI. The rate of penetration is also shown graphically in Figure V. When the acids are used

in chemical equivalents the sulfuric acid has the lowest pH and the most rapid rate of penetration. The formic acid with its high pH is slower. However, it is much faster than the straight sulfuric acid made up to a comparable pH (No. 5). The mixed-acid pickle corresponding to Stumpf's [4] formula is of course slower than the corresponding sulfuric acid pickle but faster than the formic acid pickle and with an intermediate pH as would be expected.

TABLE VI

Test No.	2	3	4	5
Water ml.	2000	2000	2000	2000
Salt g.	120	120	120	120
Delimed stock g.	40	40	40	40
Sulfuric Acid				
96.5% g.	——	20	8	.8
Formic Acid				
90% g.	20	——	12	
pH	2.28	1.01	1.40	2.36
Penetration %				
15 min.	—	50	—	—
25 min.	20	66	50	1
35 min.	40	90	60	2
55 min.	66	100	80	3
70 min.	75	—	90	4
100 min.	90	—	100	5
130 min.	99	—	—	6
pH	2.41	1.08	1.48	2.30*

* .2 g acid added during test to keep pH down.

Penetration Tests, Series No. 2

These tests were run in the penetrometer. The test pieces were in equilibrium with neutral salt solution (60 gram/1000 ml). The composition of the pickles and the results are shown in Table VII.

TABLE VII

Test No.	1	2	3	4
Water ml.	1000	1000	1000	1000
Salt g.	60	60	60	60
Delimed stock g.	10	10	10	10
Sulfuric acid 96.5% g.	10.4	17.6	18.1*	7.2
Formic acid 90% g.				10.4
Cal. Formate 99.5% g.		13.2		
Sodium Formate 95.2% g.			14.5	
Acid Equivalents	1	1.69	1.69	1.69
pH	0.83	1.01	1.10	.99
Penetration Time min.	145	180	185	180
pH	0.89	1.02	1.15	1.00

* .5 grams H_2SO_4 added to compensate for alkalies in sodium formate. (See Table I).

In this series, Tests Nos. 2, 3 and 4, all contain 1.69 chemical equivalents of acid, which is 60 per cent formic and 40 per cent sulfuric, corresponding to the Stumpf formula. In Test No. 2 the formic acid is derived from calcium formate and in Test No. 3, from sodium formate. Test No. 1 contains 1 equivalent of acid and it is all sulfuric acid. The 1 equivalent of sulfuric acid penetrates faster than the 1.69 equivalents of mixed acid, although the difference is not so great as in Series 1, when equal equivalents of sulfuric acid and mixed acids were used. (Tests 3 and 4). Tests 2 and 3 again show that like results are obtained from formic acid derived from either calcium or sodium formates, when compared with a formic acid pickle, Test 4.

While it is quite evident that formic acid pickles less rapidly than sulfuric acid, it seemed possible that due to the much greater solubility of calcium formate over calcium sulfate, that formic acid, despite its lower ionic activity, might delime faster than sulfuric acid. This would be of practical significance since it is common practice to pickle stock that is not completely delimed.

Penetration Test Series No. 3

Undelimed stock was used in these penetrometer tests as follows:

	Test No. 1	Test No. 2
Water ml.	1000	1000
Salt G.	60	60
Formic acid 90% g.	10	—
Sulfuric acid 96.5% g.	—	10
pH	2.12	0.94
Penetration time min.	400	260

This test indicates that despite the low solubility of calcium sulfate that sulfuric acid when used in equivalent concentrations delimes faster than formic acid. Here the average penetration rate for the formic acid is 65 per cent that of the rate for sulfuric acid. In Series 1, (delimed stock) the penetration rate of formic acid is only 42 per cent that of the rate for sulfuric acid. This might indicate that the solubility of calcium formate speeds up the deliming rate of formic acid but that due to its lower active acidity it is still slower than sulfuric acid.

Penetration Tests, Series No. 4

Test No. 1 from Series 3 was repeated as a control to check the action of formic acid derived from calcium formate, when used for deliming. Undelimed stock was used in these penetrometer tests as follows:

	Test No. 1	Test No. 2
Water ml.	1000	1000
Salt g.	60	60
Calcium for. g.	—	13.2
For. acid 90% g.	10	—
Sulf. acid 99.5% g.	—	10*
pH	2.12	2.21
Penetration time min.	390	390

* Slight deficiency of sulfuric acid to preclude presence of excess sulfuric acid.

The penetration times are in agreement with Series 3, Test 1, and it is evident that the formic acid derived from calcium formate delimes in a manner similar to 90 per cent commercial formic acid.

In all these penetrometer tests Series 2, 3 and 4 the penetration time is taken as the time required to bring the pH of the specimen face away from the pickle solution down to a pH of 4.0.

Summary of Penetration Tests (See Table VIII)

Summary

Various pickles—sulfuric acid, and combinations, also pickles where the formic acid has been derived from the sodium or calcium salt—are compared as to the resulting pH values, amounts of acid taken up and rates of penetrations into delimed and undelimed steer hide.

A simple apparatus for measuring penetration rates is described.

Conclusions

1. When equal chemical equivalents are used, sulfuric acid penetrates more rapidly and reacts more completely than formic acid.
2. When equal pH solutions are used, formic acid penetrates more rapidly and more acid is taken up than with sulfuric acid.
3. When mixtures are used, intermediate results are obtained.
4. The large excess of formic acid required for a satisfactory commercial pickle can be greatly reduced by using a small quantity of sulfuric acid with the formic acid. This approaches the rapid action of a sulfuric acid pickle and at the same time introduces formic acid into the pickled stock.
5. When salts of formic acid, such as sodium formate or calcium formate, are introduced into a strong acid medium—such as a sulfuric acid pickle or an acid chromium sulfate liquor—formic acid replaces an equivalent amount of sulfuric acid, with a resulting increase in pH.

TABLE VIII

Type				Pickle					Delime and Pickle			
Test No.	1-3	2-1	2-2	2-4	2-3	1-4	1-2	1-5	3-2	4-2	4-1	3-1
Acid (Sul)	100	100	40*	40**	40	40	0	100	100	0*	0	0
Ratio(For)	0	0	60	60	60	60	100	0	0	100	100	100
pH	1.0	0.83	1.01	0.99	1.10	1.40	2.28	2.36	0.94	2.21	2.12	2.12
Penetration Time Min.	55	145	180	180	185	100	130	130	260	390	390	400
Oz. penetrated	4.25	8.5	8.5	8.5	8.5	4.25	4.25	.25	8.5	8.5	8.5	8.5
Average Oz./hr.	4.6	3.5	2.8	2.8	2.7	2.5	2.0	.1	2.0	1.3	1.3	1.3
Type	Strong Sulfuric		Mixed Sulfuric — Formic				Formic	Weak Sulfuric	Sulfuric	Formic		

(*) formic acid from calcium formate

(**) formic acid from sodium formate

With the exception of Test 1-3, the penetration rate of the pickles appears to be primarily a function of pH. The high rate of Test 1-3 is probably due to the agitation during the tests in Series 1. The rates readily group themselves into strong sulfuric acid, mixed acid, formic acid, and weak sulfuric acid groups.

6. Either sodium formate or calcium formate when used with stoicheiometric equivalents of sulfuric acid is a cheap source of formic acid.
7. Such formic acid gives chemical results that appear to be identical with results obtained with commercial formic acid.
8. When the formate salts are used, reaction by-products, either sodium sulfate or calcium sulfate, are introduced into the processing liquors. While these materials are generally considered inert, they may have an effect on the pickling process or on the subsequent tanning process, and their presence must be considered.
9. The sodium sulfate formed generally stays in solution but will precipitate in cold, concentrated solution.
10. The calcium sulfate formed generally precipitates but in sufficient dilution or in presence of excess formic acid it may be completely solubilized.
11. In a mixed acid pickle, increasing the ratio of formic acid increases the solubility of calcium sulfate, and increasing the ratio of sulfuric acid decreases its solubility.

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Oak Slabs and Cordwood as a Source of Tannin and Pulp

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The present supply of domestic vegetable tannin is far short of the demand. A large proportion of it now comes from blight-killed American chestnut wood, but this source is rapidly nearing depletion. Considerable interest has

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developed in other native sources of tannin. Recent investigations have dealt with the foliage of sumacs native to the East [3], the root of canaigre native to the Southwest [4], [9], bark of hemlock, spruce and redwood of the West [16], trees of the Southeast [12], and plants native to Florida [6], more especially the scrub-oaks [2], [11]. Most of the plants processing chestnut extract are located in the Tennessee Valley region. Here the tannin producing possibilities of pine bark have been examined [14]. Oak bark has also been investigated in view of the abundance of oak in the forest [1], [15]. The present report on the separation of bark from wood in chipped oak material is the final phase of TVA investigations on use of the oak resources for the production of tannin.

The Study

Laboratory tests [1] conducted in 1944 showed that good quality leather could be made with tannin extracts obtained from oak sawmill slabs. A commercial scale test [1] made in 1946 on mill-run slabs substantiated the desirable qualities of oak extracts for heavy leather production. It was found, however, that the extract obtained from whole slabs (chestnut oak was excluded) could not compete economically with that obtained from chestnut wood at 1946 prices. It was necessary, therefore, to investigate means of lowering extraction costs. Since the tannin in oak slabs is concentrated in the bark, it was reasoned that if bark and wood could be separated, two high value products could be produced: a bark product rich in tannin and a wood product suitable for pulping. As tannin is readily leached by water, a dry unit process was sought that would permit the use of not only slabs and edgings, but also small round wood. Chipping before separation has these advantages:

1. It is applicable over a wide range of sizes of raw material.
2. The bark is removed from the wood by the shattering action of the chipper knives.
3. Removal of bark by this method will work on green or dry wood at any season of the year.

Separation of the resulting bark and wood fragments might then be accomplished by a specific gravity type of separator, provided of course that there is a difference between the specific gravity of the bark and wood. Specific gravity determinations made on a limited number of samples of oak wood and bark representing three of the more important commercial species of oak in this region are summarized in Table I. From this it may be seen that the specific gravity differential between bark and wood is of such an order that shape and size of the fragments will exert a strong influence on the separation. Hence it is necessary to screen the chipped material into several size classes before processing on the separator unit. This type of separator

segregates the chips into a series of fractions ranging from nearly pure bark at one end to nearly pure wood at the other end. Intermediate fractions are recycled with the raw material and the other fractions are recombined to form the final wood and bark products. The accompanying flow sheet (Figure 1) shows the successive steps in the process.

TABLE I

Specific gravity of wood and bark of samples of black, white, and chestnut oak*

Oak species (Quercus)	Specific gravity of—		Moisture content of—	
	Wood	Bark	Wood	Bark
Black (*Q. velutina*)	0.60	0.81	18	16
White (*Q. alba*)	.72	.90	27	20
Chestnut (*Q. montana*)	.66	.82	30	17
All	.66	.84	25	18

*This is "effective specific gravity" which was computed as the ratio of actual weight to actual volume for each sample at its moisture content. Each value is an average of 2 representative samples; moisture content is oven-dry basis.

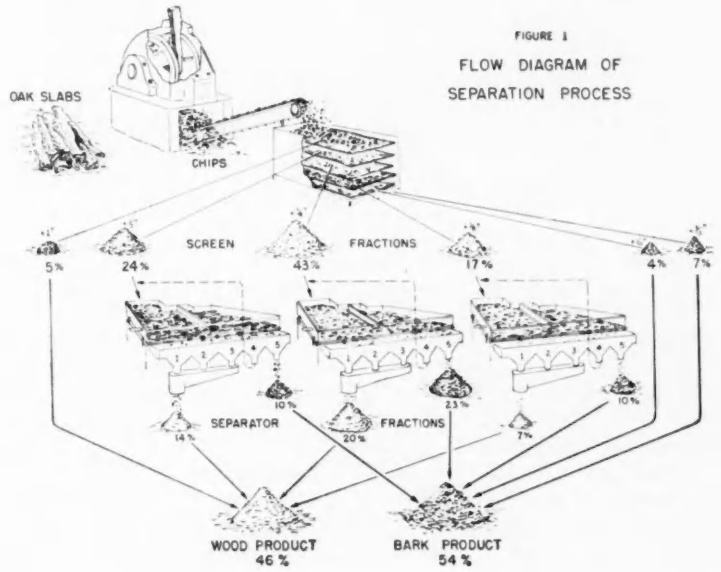

FIGURE 1
FLOW DIAGRAM OF SEPARATION PROCESS

To test the feasibility of concentrating the wood and bark of chipped oak material by this process a pilot plant was established at Norris, Tennessee in 1949.

Wood-Bark Separation Tests

In preliminary tests on local installations chips produced by a Carthage disc chipper, a drum type hog, and several V-cylinder hogs were studied for separation efficiency. The V-type sawmill hog produced the most satisfactory chips. It was equipped with an open throat type cylinder, and the throat plate was set as far below center as possible to insure maximum production of long-grained chips. The machine used in the pilot plant tests was designed by Mitts and Merrill following extensive chipping tests made at their plants. It had a 30-inch diameter, open throat V-cylinder with vertical feed and a reduced cylinder speed of 520 RPM (Figure 2). At a 1/8-inch knife setting, oak slabs were chipped at an average rate of two tons per hour, dry weight. (Table II)

TABLE II

Screen analysis of oak-slab chips produced at knife settings of 1/16", 1/8", and 3/16"*

Screen size of fractions		1/16"	1/8"	3/16"
Inches		Per cent	Per cent	Per cent
	+1	2	5	11
-1,	+½	9	24	31
-½,	+¼	38	43	40
-¼,	+1/8"	35	17	9
-1/8,	+1/12	6	4	3
-1/12,		10	7	6
All		100	100	100
Pounds per hour		1,665	3,812	—

*Oven-dry weight basis.

Because of the small differential in specific gravities of the bark and wood, the chips must be sorted into several size classes. For this operation a multiple deck reciprocating screen was designed and constructed (Figure 3). A set of five interchangeable screen decks with 1–, 1/2–, 1/4–, 1/8–, and 1/12-inch openings was used to sort the material into six size classes (Figure 1).

In the course of chipping, the bark was usually severed from the wood by the shattering action of the knives. Consequently, a high percentage of the chips were either pure bark or pure wood. Segregation of the wood and bark chips was accomplished by passing them, by size classes, over the deck of an

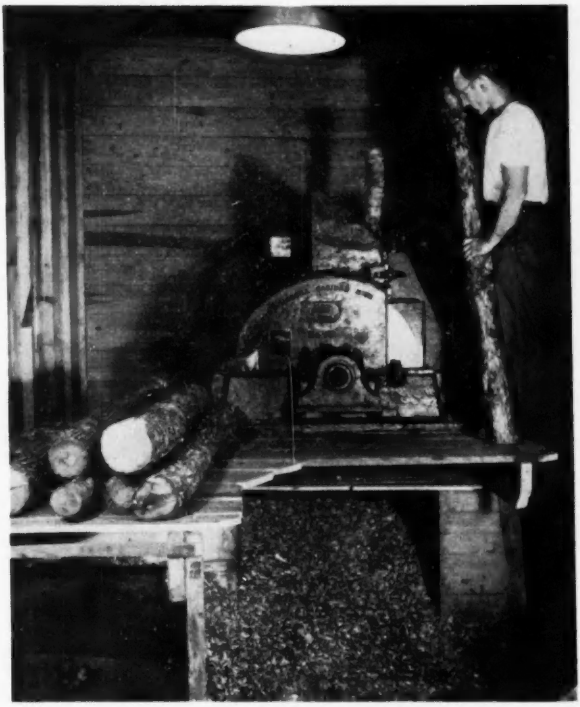

FIGURE 2—30-inch V-cylinder hog used to chip slabs, edgings, and cord wood.

air-float type specific gravity separator. For this operation a Sutton, Steele and Steele BX-100 separator, equipped with a 16-mesh per inch wire deck and low riffle bars was used. The deck was adjustable on double inclines—downward towards the discharge side and upward from the feed point (Figure 4).

A blower forced a controlled blast of air up through the deck screen under the chips causing the lighter material to rise. When properly stratified the bark remained in contact with the deck and "walked" up the incline to the far end before discharging through chute 5. The lighter wood chips rose above the bark and were freed of most of the forward kicking action of the deck. Wood chips, therefore, drifted sidewise over the riffle bars and were discharged through chutes 1, 2, and 3 (Figure 1).

It was important that chips be fed to the separator at a uniform rate. A gravity feed bin was not satisfactory. To solve this problem we built a 6-inch

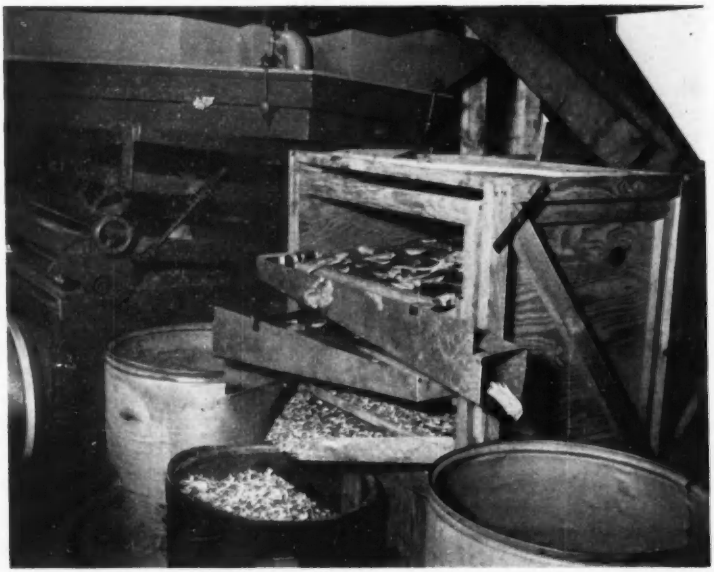

FIGURE 3—Multiple deck screen used to size chipped material.

belt conveyor, with a variable speed of from 15 to 60 feet per minute, to feed either the screen or the separator.

Raw materials tested included round oak cordwood and oak slabs and edgings. All materials were air seasoned from one to four months. Each operation was timed; total weights were taken before and after each step. Oven-dry moisture determinations were made at frequent intervals. The ratio of wood to bark was determined for each screen and separation fraction by hand sorting the bark and wood chips and weighing each separately. Separated materials were air dried to approximately 12 per cent moisture and stored until tanning and pulping tests could be run.

Preliminary chipping tests on slabs at knife settings of 1/16-, 1/8-, and 3/16-inch (distance knives project from face of V-cylinder on hog) indicated that the 1/8-inch setting was the most satisfactory. At the 1/16-inch setting the slow rate of feed resulted in an excessive quantity of fine material unsuited to pulping and thin, curled chips unsuited to separation. The 3/16-inch setting frequently stalled the cylinder, and the wood chips produced were too thick for satisfactory separation. Screen analysis of slab chips produced at the three knife settings are shown in Table II.

FIGURE 4—Air-float type of specific gravity separator and variable speed belt conveyor.

Results

Separation tests were run on both moist and air dried chips. Air dried chips stratified better on the air table, hence resulted in better separations. This is understandable because the wood chips contained more water than the bark and lost more in drying. This resulted in a greater difference in the effective specific gravities of the bark and wood. Although several discrepancies appear in Table III, it is apparent that separations are more satisfactory with dry chips than green ones.

Chipping, screening, and separation tests were run on the following types and weights (oven-dry basis) of raw materials: slabs, 2,019 pounds; edgings, 224 pounds; and cordwood, 1,374 pounds. Tables IV and V show the results of typical runs on slabs and cordwood. Chips over 1 inch in size contained very little bark; chips under 1/8 inch contained high proportions of bark. No attempt was made to further purify these sizes. Separation of the three intermediate size chips gave generally satisfactory results.

Edgings tested were long, narrow, and usually tapered. Their bark content averaged 49 per cent, somewhat higher than for either slabs or cordwood. In chipping, an excessive quantity of long strips of wood and bark from the

TABLE III

Increase in separation percentage from green to dry screened oak chips*

Oak material	Screen size of fractions		Increase in content of —			
			Bark from Chute 5	Wood from — Chute 3	Chute 2	Chute 1
	Inches		Per cent	Per cent	Per cent	Per cent
Slab	−1,	+½	11.8	6.9	4.1	4.4
	−½,	+¼	10.1	9.4	5.7	7.2
	−¼,	+1/8	5.4	− 1.8	13.0	22.4
Round wood	−1,	+½	4.2	1.0	− .1	2.0
	−½,	+¼	13.5	4.2	2.2	1.8
	−¼,	+1/8	27.5	−14.6	3.7	5.6

*Decrease in percentage is indicated by a minus sign.
Basis: 2 runs each of green and dry slabs, and 1 run each of green and dry round wood.

TABLE IV

Separation analysis per 1,000 pounds of oak-slab chips*

Screening				Separation for —							
				Bark product, Chute 5		Wood product from — Chute 3		Chute 2		Chute 1	
Size of fraction inches		Weight lbs.	Bark Content Per cent	Wt. lbs.	Bark Per cent	Wt. lbs.	Wood Per cent	Wt. lbs.	Wood Per cent	Wt. lbs.	Wood Per cent
	+1	50	5	—	—	—	—	—	—	—	—
−1,	+½	264	21	68	64	78	97	44	97	10	98
−½,	+¼	449	42	181	84	109	86	70	91	20	95
−¼,	+1/8	151	62	48	95	22	68	34	68	18	85
−1/8,	+1/12	30	84	—	—	—	—	—	—	—	—
−1 12		56	90	—	—	—	—	—	—	—	—
All		1,000**	42	297	—	209	—	148	—	48	—

*Based on June 23 run of 590 pounds of oak slabs (moisture 26 Per cent), that yielded 503 pounds of chips (moisture 10 Per cent.)
**Includes a remainder from Chute 4 of 165 pounds of un-recycled material.

tapered ends passed through the hog uncut despite a close clearance adjustment of the throat plate. As a result, a high percentage of material (approximately 12 per cent) fell in the 1-inch-and-over size class. The bark content of this size class was too high to include in the pulping product, and it could not be separated without rechipping. Rechipping is usually done in a hammermill. This produces a frayed chip that is difficult to handle by this process. The remaining normally chipped material separated with results similar to those for slabs.

TABLE V

Separation analysis per 1,000 pounds of oak-cordwood chips*

Size of fraction inches		Screening Weight lbs.	Screening Bark content Per cent	Separation for — Bark product Chute 5 Wt. lbs.	Bark product Chute 5 Bark Per cent	Wood product from — Chute 3 Wt. lbs.	Chute 3 Wood Per cent	Chute 2 Wt. lbs.	Chute 2 Wood Per cent	Chute 1 Wt. lbs.	Chute 1 Wood Per cent
	+1	60	2	—	—	—	—	—	—	—	—
−1,	+½	205	6	43	15	60	98	38	97	12	99
−½,	+¼	462	21	88	45	105	90	133	89	45	93
−¼,	+1/8	200	36	29	78	45	65	64	80	26	85
−1/8,	+1/12	31	52	—	—	—	—	—	—	—	—
−1/12		42	80	—	—	—	—	—	—	—	—
All		1,000**	24	160	—	210	—	235	—	83	—

*Based on June 29 run of 572 pounds of oak roundwood (moisture 50 Per cent), that yielded 420 pounds of chips (moisture 13 Per cent).

**Includes a remainder from Chute 4 of 179 pounds of un-recycled material.

Costs of chipping, screening and separation in terms of kilowatt hours per ton based on averages obtained in the pilot plant tests are given in Table VI. Recent correspondence with the manufacturer of the separator indicates that its capacity can be increased by equipping it with a deep tailing riffle and making certain adjustments. Likewise, a commercial screen would be much more efficient than the experimental model used in these tests. In a commercial operation the chipping, screening and separation steps would be conducted simultaneously. This, with an adequate conveyor system, would further reduce unit costs to an economical figure.

TABLE VI

Cost of chipping, screening, and separating one ton of oak slabs*

Material (one ton)	Machine Kind	Machine HP	Operation time	Power cost
			machine hrs.	KW hrs.
Slab	Hog	20	0.42	6.27
Chips	Screen	¼	4.66	.87
Chips	Conveyor	1	4.66	3.48
Chips	Separator	10	5.56	41.48
Chips	Conveyor	1	5.56	4.15
				56.25

Total power cost —1c per KW hr. 56c per ton.

*Based on averages of pilot plant runs on slabs. Comparable chipping rates for cordwood and edgings were 0.35 and 0.83 machine hours, respectively.

In this study all material was processed into two products: (1) a material of high bark content suitable for tannin extraction and (2) a material of high wood content suitable for pulping. The five fractions from the separator ranged from a concentration of wood in chute 1 to a concentration of bark in chute 5; intermediate fractions had appreciable amounts of both materials. One fraction (chute 4) contained approximately the same proportion of bark and wood as the original material and was recycled with the raw feed to the separator. Materials from chutes 1, 2, and 3, plus the material held on the 1-inch screen, were combined to form the pulping product. The fraction from chute 5, and all minus 1/8-inch material, made up the bark product. A summary of the two products obtained by recompositing is shown in Table VII.

TABLE VII

Composition of final bark and wood products obtained after air separation

Material and condition	Slabs		Cordwood	
	Green	Dry	Green	Dry
Chips, unseparated				
Moisture content....per cent	22	12	35	13
Bark content.....per cent	40	43	21	22
Quantity processed..lbs.*	1384	635	1014	360
Bark product				
Per cent in terms of total chips	51	54	26	26
Bark content.....per cent	65	72	40	53
Bark recovery.....per cent	89	90	56	65
Wood product				
Per cent in terms of total chips	49	46	74	74
Wood content.....per cent	90	91	89	90
Wood recovery.....per cent	68	74	81	84

*Oven-dry weight basis.

Follow-up tests were made to determine suitable commercial outlets for the two products produced. The bark product was tested through the cooperation of J. S. Rogers*. Tests included tannin analysis, extraction studies and the tanning of heavy leather samples with the extracts so obtained. Although the 6.5 per cent tannin found in the bark product is lower than if chestnut oak had been included, results of the tests further substantiated the fact that tannin from oak bark produces heavy leathers of good quality.

The Laboratory also conducted tannin analyses on pure bark samples that we collected from eight species of oaks commercially important in the Tennessee Valley. From results of these tests Rogers reports [10] the tanning content as ranging from a high of 15.6 per cent for chestnut oak to a low of 5.9 per cent for Northern red oak.

*J. S. Rogers, Head, Division of Hides, Tanning Materials, and Leather; Eastern Regional Research Laboratory, U.S.D.A., Philadelphia, Pa.

Samples of the wood product were submitted to the Forest Products Laboratory, Madison, Wisconsin, for tests to determine its pulping characteristics**. These tests[5] included pulping the wood product to a yield of 78 per cent by the semi-chemical, neutral sulfite process. Both the pulp and the corrugating board made from it were found to be below commercial strength standards. However, on the basis of earlier experiments with spent oak chips[1] and experiences with other species, the Laboratory states that a commercially acceptable product can be produced by pulping this material to a yield near 70 per cent. They further indicate that it should be economically feasible to produce pulp in this relatively low yield. The properties of corrugating boards made from oak slabs after pulping by the semi-chemical, neutral sulfite process are compared with various commercial boards in Table VIII. This comparison indicates that oak slabs, when pulped to a near 70 per cent yield, will produce boards with properties which compare very favorably with commercial boards. The use of oak alone, and in blend with pine, for corrugating board has been reported by Sapp[13]. His mill scale experiments showed that when oak pulp is blended with as little as 7½ per cent pine pulp, the oak pulp was only slightly inferior to that produced from the gums.

**These tests at the Forest Products Laboratory, Madison, Wisconsin, were conducted in the Division of Pulp and Paper, G. H. Chidester, Chief.

TABLE VIII

Properties of corrugating board made from oak slabs after pulping by semi-chemical neutral sulfite process compared with commercial boards*

Material	Pulp yield	Weight per 1000 sq. ft.	Thickness	Bursting strength	Tearing strength	Compression resistance
	Per cent	lbs.	in.	pts. /lb. per rm. **	gms./lb. per rm.**	lbs.
Oak slab—						
Wood product (present test)	78.0	26.1	0.0113	23	0.73	33.6
Spent chips, screened***	78.9	25.9	.0091	20	.47	8.4
Spent chips, screened***	72.5	31.2	.0094	35	.72	16.7
Commercial—						
Straw-board	——	34.0	.0110	20	.97	10.0
Chestnut-board	——	26.6	.0089	27	.58	7.6
Hardwood-board	——	27.4	.0100	38	1.00	49.6

*Based on results of tests conducted by the Forest Products Laboratory, Madison, Wisconsin.
**Ream weight basis, 25 x 40 – 500.
***Material remaining on a 14-mesh screen from 1946 tannin-extraction test on un-separated oak slab(1).

Discussion

In any processing operation the value of the products must be balanced against costs. When working with a waste product, such as oak slabs, it is important to market all processed material and avoid producing a secondary waste. Although this study was aimed at producing a tannin product, and a pulping product, it does not preclude the use of certain fractions for other purposes. In fact, the disposal of certain fractions through other outlets would definitely improve the quality of both of the proposed wood and bark products. McIntyre [7] has suggested such nonpulping uses for wood chips as animal bedding, poultry litter, compost and soil conditioner, mulch for orchards and berries, soil covering for yards, grounds and roads, and packing material.

An evaluation of the wood-bark separation process as outlined in this paper may be expressed in terms of the increase in value of the separated products as compared to the value of slabs for fuel. As compared to the extraction of whole slabs the advantages of separation lie in the production of (1) a valuable bark product that yields nearly as much tannin which costs less to extract, and (2) a valuable wood product for pulping.

To arrive at the value of a ton of processed slabs, we will first consider the bark product. This was found to contain 54 per cent of all the material and 90 per cent of all the bark. The tannin content as determined by Rogers [10] was 6.5 per cent. In a commercial operation an extraction efficiency of 75 per cent should be attainable without an undue decrease in extract purity. Therefore, from a ton of air-dry slabs (15 per cent H_2O) we could expect 918 pounds of moisture free bark product. From this, 45 pounds of tannin can be recovered which at 14 cents per pound (1946 price) will make a tannin value of $6.30 for the bark product obtained from a ton of slabs. At 60 per cent moisture the spent bark chips will have a fuel value equivalent to one-sixth ton of coal, or approximately $1.25. To this must be added the value of the 46 per cent of the material falling in the wood product which has been found by test to be suitable for pulping. At an estimated value of $10.00 per ton for this low bark content, chipped material, an additional $4.60 will be added to make a total value of $12.15 for the processed products obtained from a ton of air-dry slabs.

To arrive at the cost of raw material and processing we will take the value of a cord of air-dry slabs (3750 pounds @ 15 per cent H_2O) at $8.00, as obtained in the commercial test [1]. Converting to a tonnage basis will make the cost of slabs $4.27 per ton. From this same test combined chipping and extraction costs are reported at $6.85 per cord, or $3.65 per ton of slabs. As the breakdown on chipping cost alone is not available for this test, reference is made to Morgan's [8] very comprehensive study of the cost of producing chips from cull and waste wood. From his report and information obtained in this

pilot plant study, the chipping cost is estimated at $1.10 per ton. As all the material must be chipped anyway, there will be no savings at this point. However, as the bark product represents only 54 per cent of the chipped material and has a higher tannin content than whole slabs, the extraction costs should be reduced by nearly a half. Therefore the extraction cost of $2.55 for whole slabs would be reduced to $1.38 for the bark product for a ton of slabs.

On the basis of our experience in the pilot plant tests we estimate that a commercial plant chipping 50 tons of sawmill waste per day could screen and separate the wood from bark at a cost of $1.35 per ton. This estimate is based on a capital investment at 6 per cent interest covering commercial screens, a series of separators and the necessary conveyor units to fully mechanize chip handling. Power costs are based on $ .01 per kilowatt-hour and labor costs are based on a minimum rate of $1.00 per hour.

Summarizing the costs of raw materials and processing we get the following:

1 ton air-dry slabs	$4.27
Chipping costs per ton slabs	1.10
Extraction cost for bark product	1.38
Screening and separation costs	1.35
Total cost of one ton of air-dry material and processing	$8.10

Similarly the value of the processed products are:

Tannin recovered from bark product from one ton of slabs	$6.30
Fuel value of spent chips	1.25
Allowed for value of wood product	4.60
Total value of one ton of air-dry slabs	$12.15

The difference between these two values represents the amount available for transportation, sales expenses and other items not mentioned. It should be kept in mind that the high tannin content of chestnut oak bark normally included in mixed oak slabs would further raise the value of the bark product.

Summary

Laborary and commercial scale studies were initiated by TVA in 1944–45 [1] to determine the suitability of oak sawmill waste as a local source of vegetable tannin to supplement diminishing supplies of chestnut wood. Heavy leather of good quality was produced with this oak extract. However, the cost per tan unit was slightly higher than for chestnut wood. To reduce this cost differential a pilot-plant study was made at Norris, Tenn., to determine the feasibility of separating the bark and wood from chipped oak waste prior to extraction. As compared to extracting whole chipped oak

slabs the advantages in wood-bark separation would be production of (1) a wood product suitable for pulping and (2) a bark product yielding nearly as much tannin but costing only about half as much to extract. The process includes chipping and screening operations followed by separation on a specific gravity type, air-float separator. Satisfactory separation was obtained when the chips were correctly cut and carefully sized by screening prior to actual separation. Tests of different styles of chippers, indicated the V-cylinder, open-style throat, sawmill hog to be most satisfactory for separations by this process.

Raw materials tested included mixed oak slabs, edgings, and cordwood. Chestnut oak was excluded because it is already an accepted source of tannin. Edgings proved inferior to slabs because they could not be chipped satisfactorily. Although the separations on cordwood were not as efficient as on slabs, we believe that cordwood could be processed satisfactorily if chipped on a large diameter hog. Better separation was achieved with air-dried chips than with green ones.

The various fractions obtained by separation were recombined according to their bark content into two products: (1) a bark product for tannin extraction, and (2) a wood product for pulping. Tests on the bark product showed it to contain sufficient tannin to make its commercial extraction feasible. Heavy leather produced with this extract was of good quality. Pulping tests made on the wood product showed that it would be economically feasible to produce an acceptable quality corrugating board from this material.

Estimates from these and earlier tests indicate that slabs can be purchased, chipped, screened and separated for approximately $8.00 per ton. The processed products from a ton of slabs have an estimated market value of $12.00. In view of these test results and the continued demand for vegetable tannin, use of oak slabs and cordwood as a source of tannin and pulp in the Southeast appears to warrant further consideration.

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ABSTRACTS

The Neutral Salt Effect In Chrome Tanning. By S. G. Shuttleworth. *J. Soc. Leather Trades Chemists*, **36,** 34 (1952). Gustavson believes he has given evidence that the retarding and decreasing effect of neutral sulfates on chrome fixation by collagen, from solutions of basic chromium sulfate, is mainly due to the conversion of electropositive chromium into uncharged complexes which possess a lower degree of affinity for collagen. Wilson has shown that the effect of neutral salts can be related to the hydration of the salt. Küntzel, Riess and Stiasny consider that the neutral salt causes dehydration of the protein, thus limiting accessibility of the reactive groups. The writer found no effects upon the rates of reaction between chrome alum and sodium acetate from the addition of sodium sulfate, using a solvent extraction method. The object of the present work is to provide additional evidence on the subject. The effect of heat at different time durations was studied by tanning with 7 per cent solution of one-third basic chromium sulfate, with and without sodium sulfate additions, for 3 hours and 24 hours, making the additions to cold chrome liquor and to a liquor boiled immediately preceding additions. It was evident from the results that the sodium sulfate effect was the same whether added to the cold or hot chrome liquor prior to tannage. The effects of sodium sulfate addition to chrome sulfite tannage (anionic complexes) and chromium formate tannage (cationic complexes) were compared under similar conditions. Also anionic complexes were prepared by boiling one-third basic chromium sulfate with sodium oxalate and sodium sulfate. All three types of chromium complexes, both cationic and anionic, showed similar neutral salt effects. The author accepts this as evidence against Gustavson's explanation. A comparison of a carboxy type base exchange resin (wofatit C) with hide powder was made, using a 24-hour tannage at 25 degrees C. and varying amounts of sodium sulfate addition. It was assumed that, if Gustavson's explanation is correct, the neutral salt effect on the base exchange resin should be just as great as upon the hide powder. Actually it was only about half as much, again indicating that the effect is not due to change in electric charge. The writer has been unable to find any examples in the literature where a proved change in the degree of coordination has been found

to cause no change of color in a solution of a chromium complex. Therefore spectrophotometric evidence was sought. Results showed that sodium sulfate additions had no marked effects either on the color of one-third basic chromium sulfate complex or on the rate of its reaction with sodium acetate. The various complexes formed were checked electrophoretically and it was found that the addition of sodium sulfate had the effect of reducing the extent of their migrations, in proportion to the quantity added, but did not alter the direction of migration. Benzidine hydrochloride analyses demonstrated that there was no appreciable disappearance of sulfate into the chromium complex through addition of sodium sulfate. Following a discussion of the results of this work in relation to Gustavson's assumptions, the author concludes that the so-called "neutral salt effect" is due to reduced accessibility of the reactive protein centers caused by the lyophilic character of the salt, and to the saturation of minor electric charges responsible for that portion of the chromium fixed by residual valency forces. R. H. T.

Tannins. III. The Fractionation of Mimosa Extract. By K. S. Kirby, E. Knowles and T. White. *J. Soc. Leather Trades' Chemists*, **36,** 45 (1952). Previous work has shown that catechol, resorcinol and pyrogallol are all present in the components of mimosa extract, even in the so-called purified separation. However, claims have been made that mimosa has been purified by solvent extraction or other means producing a single tannin. A suggested formula for this isolated tannin has been offered. To secure further evidence on this subject mimosa was fractioned by solvent fractionation and by counter current distribution in systems of immiscible solvents. The entire extract and all fractions were examined by two way chromatography. For solvent fractionation the dried mimosa was first extracted with acetone. The residue was extracted with methanol. The insoluble residue was the fraction with the lowest tannin content. The methanol soluble portion was next lowest. The acetone soluble fraction was partially precipitated with ether in ratio of nine ether to one acetone. The residue was taken as a fraction and the soluble portion dried, redissolved in acetone and again precipitated with ether. The soluble portion was retained as a fraction. The residue was again dissolved in acetone and precipitated with ether. Both residue and soluble portions were kept as fractions. Thus six fractions were obtained. They varied in pH from 3.7 to 5.5 and in tannin content from 24.7 to 89.7 per cent. The chromatographs, freshly sprayed with bis-diazotized benzidine or ammoniacal silver nitrate, shower the presence of at least 27 different polyphenolic substances pretty well distributed throughout the fractions. For the immiscible solvent extractions the following systems were used: ethyl acetate/water, butanol/acetic acid/water (5:1:4), ether/acetone/water (5:1:4). In this case also the fractions showed the large number of substances distributed more or less throughout all fractions. In no case were all the substances found in any one fraction nor was there any fraction made up of only one substance. All experimental procedures are described. The presence of at least 27 probable phenolic substances capable of reacting with ammoniacal silver nitrate or bis-diazotized benzidine has been established. There were 10 other components made evident by their fluorescence in ultra violet light. The extreme complexity of the extract is thus established. Previous claims that "pure" mimosa tannin has been isolated and its structure demonstrated are shown to be incorrect. It is made evident that the extract contains a number of tannins, no one of which can be treated as the characteristic mimosa tannin or assigned a known chemical structure. R. H. T.

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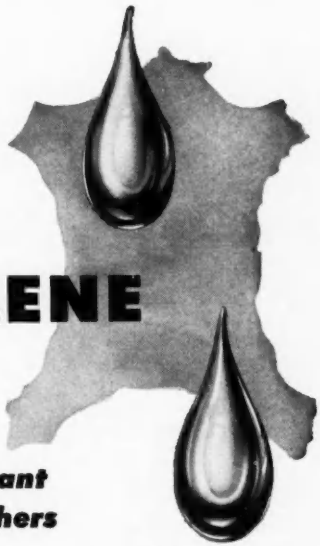

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